Properties of Perfluorobenzene near the Critical Point[1]

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The density of vapor and liquid perfluorobenzene along the liquid–vapor coexistence curve has been studied by a gamma-ray attenuation technique over the temperature range from 299 to 517 K. According to measurements, the coordinates of the critical point are $T_C = 516.66 \pm 0.05$ K and $\rho_C = 550.5 \pm 2$ kg·m^{-3}. The critical exponent β of the coexistence curve equals 0.343 ± 0.005, which agrees closely with the non-classical value. The results of our measurements were compared with data available in the literature. The height dependence of the density of a two-phase sample was investigated in relation to the temperature and time. These experiments made it possible to determine the isothermal compressibility of liquid and vapor phases near the critical point.

KEY WORDS: critical exponent; critical point; density; gamma densimeter; gravitational effect; isothermal compressibility; liquid and vapor phases; perfluorobenzene.

1. INTRODUCTION

A knowledge of the properties of fluoroorganic liquids (FOLs) near the critical point is of great interest in many fields of science and industrial practice. The density (ρ) is one of the most important characteristics of matter. Data on the density are necessary for the development of an equation of state and determination of different physicochemical properties. The purpose of this work is to demonstrate the perfomance of the gamma-ray attenuation technique for studying thermal properties of FOLs in the critical region

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and to obtain precise experimental data on the density of perfluorobenzene for both liquid and vapor states. The gamma-ray attenuation technique was previously used to study thermal properties of high-temperature melts and freons [1–3]. The basic advantages of this method are it's contact free, universal and, in particular, it gives the possibility of direct measurement of density changes during the liquid–vapor phase transition.

2. EXPERIMENTAL

Measurements of the density of perfluorobenzene (C_6F_6) were carried out on a P-2 gamma-densimeter of the Institute of Thermophysics SB RAS [4], equipped with a new measurement cell, which was specially designed by the authors for these experiments (Fig. 1). For the gamma-ray source, we use ^{137}Cs isotope having an activity of 50 GBq and a photon energy of 662 keV. The narrow beam of gamma quanta penetrates through the cell containing the two-phase system. The intensity of transmitted radiation is measured with a scintillation counter. The experimental cell is a thick-walled stainless-steel cylinder, 40 mm in internal diameter and 140 mm in length. The face planes of the cylinder are closed with stainless-steel caps. The volume is connected with a filling vessel, liquid level regulation system, and vacuum pump by means of an arrangement of valves. The cell is placed in a dry thermostat. The temperature in the thermostat is maintained within ± 5 mK throughout the measurements. The lifting gear allows for vertical movement of the installation with respect
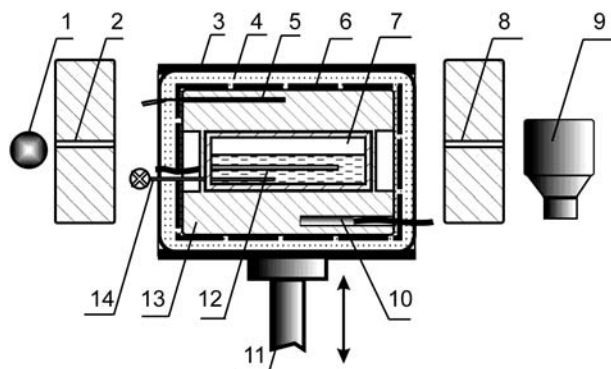

Fig. 1. Basic schematic of the gamma densimeter. 1 – gamma ray source (^{137}Cs); 2, 8 – collimators; 3 – body; 4 – heat-insulating layer; 5 – thermocouple; 6 – heater; 7 – cell; 9 – scintillation counter; 10, 12 – Pt resistance thermometers; 11 – lifting gear; 13 – thermostating block (duralumin); 14 – tube with valve.

to the beam and, thus, for measurements of the gamma-ray attenuation in the sample in relation to the distance from the cell bottom (h). This makes it possible for concurrent measurements of the densities of two equilibrium phases along the coexistence curve. The temperature of the samples is measured on ITS-90 with a 50 Ω platinum resistance thermometer (12 in Fig. 1) calibrated at the Siberian Scientific Research Institute of Metrology, Novosibirsk. The uncertainty of the temperature, including the uncertainty of the calibration and the temperature gradients, does not exceed $\pm 0.05\,\mathrm{K}$.

The density of the sample is determined from the expression [1],

$$\rho(T) = \frac{\ln\left[J_0(T)/J(T)\right]}{\mu l_{293}\left[1 + \alpha(T)(T - 293)\right]} \tag{1}$$

where T is the temperature and l_{293} is the attenuation length at 293 K, $\alpha(T) = (l(T) - l_{293})/[l_{293}(T - 293)]$ is the mean linear coefficient of thermal expansion of the cell material [5], $l(T)$ is the attenuation length at T, $J_0(T)$ and $J(T)$ are the intensities of the radiation after passage through the empty and filled (with a sample) measurement cell, respectively, and μ is the mass attenuation coefficient of the investigated substance, which is dependent on its chemical composition but is not dependent on temperature and pressure.

Provided that the density of the liquid ρ_0 is known at a temperature T_0 (as a rule, this temperature is close to 293 K), one may use the relative version of the method and calculate the density from the expression,

$$\rho = \rho_0\,(T_0)\,\frac{\ln[J_0(T)/J(T)]}{\ln[J_0(T_0)/J(T_0)]}\,\frac{[1 + \alpha(T_0)(T_0 - 293)]}{[1 + \alpha(T)(T - 293)]} \tag{2}$$

A detailed description of the procedure for measuring $J_0(T)$, $J(T)$, "dead time" of the counting channel, etc. is given in [1, 2], and [4].

To estimate unaccounted systematic errors, we measured the density of distilled de-aerated water by the relative version of the gamma method. The reference data on the water density were obtained from [6]. These experiments have shown that the experimental errors of the liquid and vapor densities fall within ± 1 to $1.5\,\mathrm{kg \cdot m^{-3}}$ over the temperature range from 293 to 523 K.

If the measurement of the reference density ρ_0 with another method presents difficulties (as a rule, because of high vapor pressure) and the literature data are not sufficiently reliable, there is a need to use the absolute method, which means determining the mass attenuation coefficient of the matter. The value of μ can be found from the expression,

$$\mu = \sum \mu_i c_i \tag{3}$$

where μ_i and c_i are the mass attenuation coefficients and the mass concentrations of the elements in the compound, respectively. Our experience suggests that using literature values of μ_i may introduce an error up to 1–3% into the determined density. The error can be significantly reduced by using experimental values of μ_i measured with the same gamma densimeter. To determine the mass attenuation coefficients of carbon, fluorine, hydrogen, and oxygen, the mass attenuation coefficients of water (H_2O), heptane (C_7H_{16}), toluene (C_7H_8), and perfluorobenzene (C_6F_6) had been measured. The values of μ_i of the elements were found by solving the equation set of Eq. (3). Next, these values were used to calculate the mass attenuation coefficients of several FOLs with low vapor pressures at room temperature: 2,2,3,3-tetrafluoro-propanole-1 ($C_3F_4H_4O$), perfluorotoluene (C_7F_8), and perfluorodibutyl ether ($C_8F_{18}O$). The difference between the data on the density of these substances obtained by the gamma method (absolute version) and the Archimedean method was less than 0.15%. Consequently, the accuracy of the absolute variant of the gamma method is quite comparable with the accuracy of relative measurements based on the condition that experimental values of μ_i are used.

3. RESULTS AND DISCUSSION

The perfluorobenzene sample was supplied by the Novosibirsk Institute of Organic Chemistry SB RAS with a stated minimum purity of 99.67 mol%. The main impurities were pentafluorobenzene (0.3 mol%) and pentafluorochlorobenzene (0.03 mol%). Before the experiments, the initial product was purified further by boiling for the purpose of removing dissolved gases and volatile components.

The density was measured along the liquid–vapor coexistence curve. In these measurements, the relative version of the gamma-ray attenuation method was used. The value of ρ_0 for the liquid density at room temperature was measured by the indirect Archimedean method with an uncertainty better than 0.03%.

Before proceeding to the results of the density measurements, let us cover some peculiarities of these experiments. As already noted, the gamma densimeter allows us to measure the height dependence of the density of a two-phase sample. This makes it possible to observe the so-called hydrostatic (or gravitational) effect connected with the high compressibility of the sample near the critical point of the liquid–vapor coexistence curve. The effect manifests itself in that the densities of the phases become height-dependent when the temperature is close to the critical value, see Fig. 2. This phenomenon was observed at temperatures above 514 K. To determine the densities of the liquid and vapor in equilibrium with each
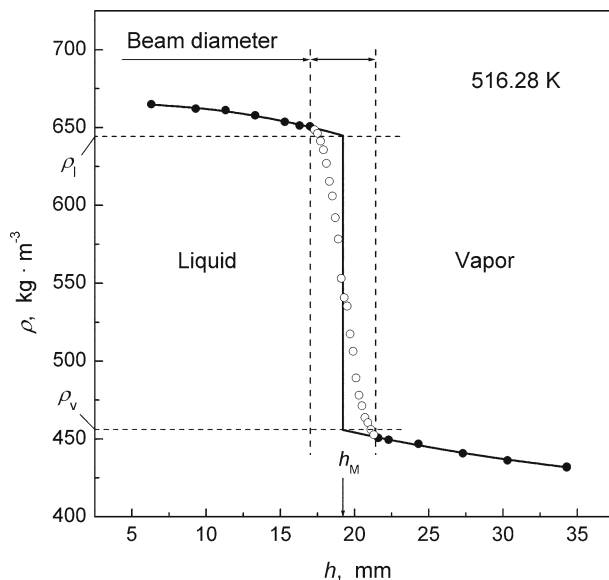
Fig. 2. Height dependence of the density of two-phase sample of perfluorobenzene at 516.28 K. Solid and open circles are experimental data. h_m is the interface location. Solid line represents real density profile derived from the procedure, which is described in the main text. ρ_l and ρ_v are the densities of the liquid and vapor phases in equilibrium.

other, we must extrapolate to the two-phase interface. On the other hand, since the diameter of the gamma-ray beam is a 4.4 mm, the stepwise density change occurring in passing through the interface appears as a continuous transition taking place in the height interval equals to the beam width (open circles in Fig. 2). The following procedure was used for determination of the meniscus location, h_M, and the densities of the equilibrium phases. The observed density profile over the region of its drastic change was fitted with a polynomial. It can be easily shown that the $d\rho/dh$ derivative has a maximum value when the axis of the gamma-ray beam passes through the phase boundary. This distance was taken as the meniscus location, h_M. The densities of the liquid (ρ_l) and vapor (ρ_v) phases in equilibrium with each other were determined by extrapolation of the approximate height dependences of the liquid $\rho_l(h)$ and vapor $\rho_v(h)$ densities (solid lines in Fig. 2) to h_M.

In Table I and Fig. 3 are given the temperature dependences of the present experimental densities of liquid and vaporous perfluorobenzene

Table I. Experimental Orthobaric Densities
of Perfluorobenzene

T (K)	ρ_l (kg$\cdot$m^{-3})	ρ_v (kg$\cdot$m^{-3})
298.79	1605.4	–
323.83	1548.5	2.3
343.88	1499.4	–
363.85	1450.5	–
383.91	1397.9	15.5
403.92	1342.1	25.8
423.93	1281.2	40.6
443.90	1213.9	62.7
463.89	1135.3	95.3
483.90	1037.1	146.7
493.93	974.0	186.0
503.88	892.3	243.5
508.90	835.8	287.0
513.91	744.6	363.5
513.92	746.3	363.5
515.98	670.3[a]	433.7[a]
516.28	644.8[a]	455.8[a]
516.57	610.1[a]	491.5[a]

[a] Value was obtained by extrapolation (see
text).

along the coexistence curve. Notice that the vapor densities at 323.83
and 383.91 K agree with the ideal gas density ρ_v^{id}, within the estimated
uncertainty;

$$\rho_v^{id} = \frac{P_S M}{RT} \tag{4}$$

where P_S is the saturated vapor pressure [7], $M = 186.05462$ kg$\cdot$kmol^{-1} is
the molar mass of perfluorobenzene [8], and R $= 8.314472$ J$\cdot$mol$^{-1}\cdot$K^{-1}
is the universal gas constant [9].

According to a recent study on the nature of critical phenomena [10],
the asymptotic behavior of the liquid–vapor coexistence curve in the vicin-
ity of the critical point is described by

$$(\rho_l - \rho_v) = A\varepsilon^\beta \tag{5}$$

Here, $\varepsilon = 1 - T/T_C$, T_C is the critical temperature, A is a constant, and β
is the critical exponent of the coexistence curve. To determine β and T_C,
data for the density (Table I) over the range of ε from 1.8×10^{-4} to 0.10
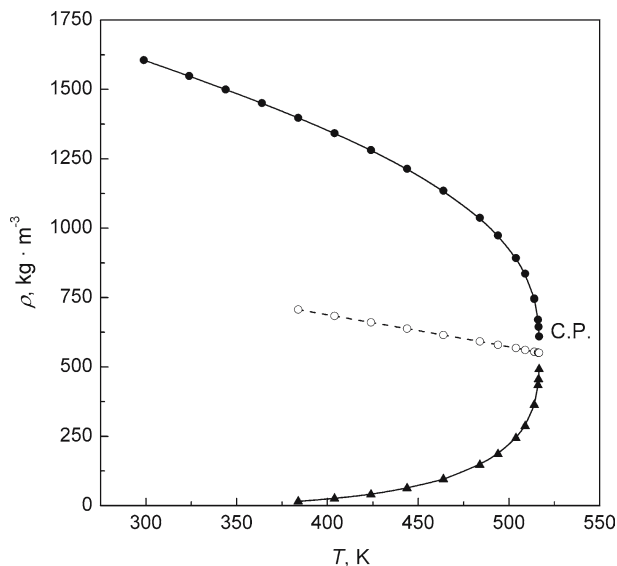were fitted with Eq. (5), where $A = 2299.69$ (see Fig. 4); then,

Fig. 3. Orthobaric densities of perfluorobenzene along the liquid–vapor equilibrium line. Solid circles and triangles are the experimental points for liquid and vapor phases, respectively. Open circles are the midpoints of the coexistence curve.

$$T_C = 516.657 \pm 0.050 \, \text{K} \quad \text{and} \tag{6}$$

$$\beta = 0.343 \pm 0.005 \tag{7}$$

The total uncertainty is listed for the critical temperature and critical exponent. Random errors of T_C and β are $\pm\,0.005\,\text{K}$ and $\pm\,0.002$, respectively. The obtained value of the critical temperature agrees with literature values of $T_C = 516.67 \pm 0.02\,\text{K}$ [11] and $T_C = 516.47 \pm 0.2\,\text{K}$ [12], to within the estimated uncertainty. The present critical exponent value is close to the non-classical value of β calculated from the Ising model; according to various methods, the calculated value lies in the range of 0.31 to 0.34 [10].

To determine the critical density (ρ_C), experimental data over the temperature range from 383.9 to 516.6 K were fitted by the following equation [10]:

$$(\rho_l + \rho_v)/2 = \rho_C + B_1 \varepsilon^{1-\alpha} + B_2 \varepsilon \tag{8}$$

where $\alpha = 0.11$ is the critical exponent for the heat capacity [10], $B_1 = 232.295 \, \text{kg} \cdot \text{m}^{-3}$, $B_2 = 336.586 \, \text{kg} \cdot \text{m}^{-3}$, and

$$\rho_C = 550.5 \pm 2.0 \, \text{kg} \cdot \text{m}^{-3} \tag{9}$$
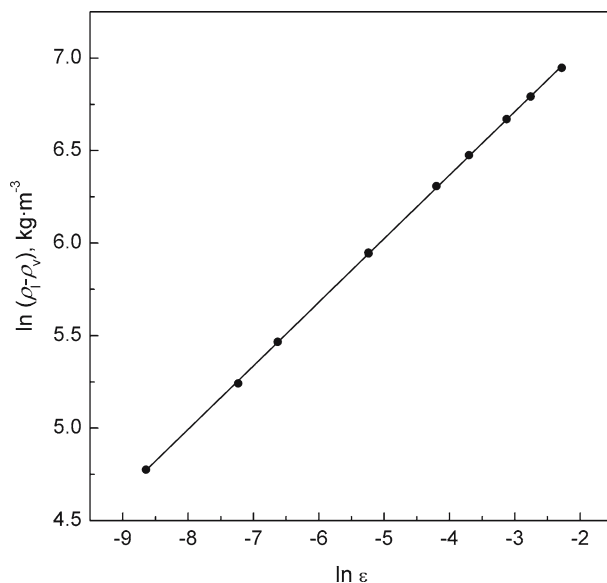
Fig. 4. Dependence of $\ln(\rho_l - \rho_v)$ on $\ln(\varepsilon)$ along the coexistence curve. Circles are experimental points. Line represents Eq. (5).

A random error of ρ_C is $\pm\ 0.2\,\text{kg}\cdot\text{m}^{-3}$. The present critical density value is in good agreement with the result of Hales and Townsend [13] ($\rho_C = 550.4\,\text{kg}\cdot\text{m}^{-3}$) and is slightly less than the result of Douslin et al. [11] ($\rho_C = 555.2 \pm 2.8\,\text{kg}\cdot\text{m}^{-3}$). The data for the density of the liquid and vapor phases along the coexistence curve were fitted with the Eq. [2],

$$\rho_{l,v} = 550.5(1 + C_1\varepsilon^{0.343} + C_2\varepsilon^{2/3} + C_3\varepsilon + C_4\varepsilon^{4/3}) \tag{10}$$

where $C_1 = -2.061135$, $C_2 = -0.211723$, $C_3 = 1.585351$, and $C_4 = 0$ for the vapor phase and $C_1 = 2.000181$, $C_2 = 0.894630$, $C_3 = -0.972266$, and $C_4 = 1.059527$ for the liquid phase.

Equation (10) describes the experimental data with standard deviations of $\pm 0.3\,\text{kg}\cdot\text{m}^{-3}$ and $\pm 0.8\,\text{kg}\cdot\text{m}^{-3}$ in the temperature ranges from 383.9 to 516.6 K and 298.8 to 516.6 K for the vapor and liquid, respectively. Figure 5 shows the results of our measurements in comparison with literature results [11, 13]. Probably, the remarkable discrepancies near the critical point are due to ignoring the corrections for density gradients in [11]. The data for the densities of saturated vapor and liquid make it possible to calculate the enthalpy of vaporization (ΔH_{vap}) using the Clausius–Clapeyron equation. For this purpose, the literature data on the saturated
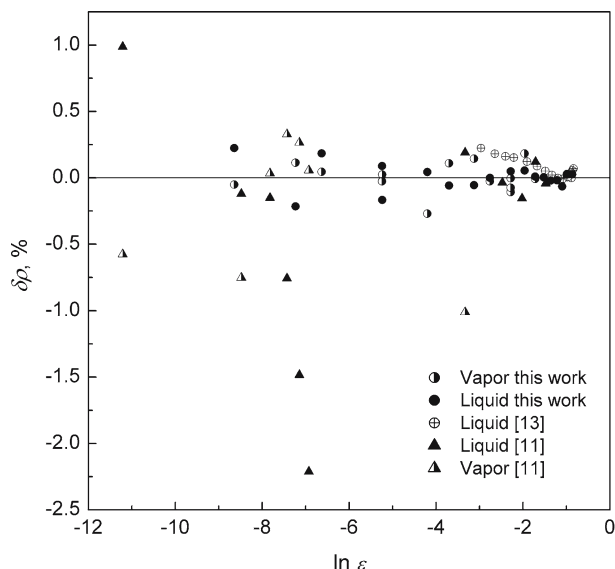
Fig. 5. Deviations (in %) of literature data for the density of perfluorobenzene along the coexistence curve from Eq. (10); $\delta\rho = 100[\rho_{l,v} \text{ (Ref.)}/\rho_{l,v} \text{ (Eq. 10)} - 1]$.

vapor pressure [7, 11] in the range from 278 K to T_C were approximated by the empirical equation,

$$\ln(P_S) = \left(D_1\varepsilon + D_2\varepsilon^{1.25} + D_3\varepsilon^3 + D_4\varepsilon^7\right)\frac{T_C}{T} + D_5 \qquad (11)$$

where $D_1 = -8.432480$, $D_2 = 1.685919$, $D_3 = -3.476787$, $D_4 = -7.775381$, and $D_5 = 8.093499$.

Equation (11) describes the data [7, 11] with a standard deviation of $\pm 0.02\%$. The normal boiling temperature T_B was determined by extrapolating Eq. (11) to the pressure 101.325 kPa. The obtained value ($T_B = 353.41$ K) coincides with that of Counsell et al. [14]. A summary of the calculated thermodynamic properties for perfluorobenzene along the coexistence curve is given in Table II.

Figure 6 shows the results of our measurements of the sample density near the critical point in relation to the distance from the meniscus. These data make it possible to estimate an isothermal compressibility of perfluorobenzene in the liquid and vapor phases. A hydrostatic pressure was calculated from the following expressions:

Table II. Calculated Values of Thermodynamic Properties of Perfluorobenzene along the Coexistence Curve

| T (K)	P_S(kPa)	ρ_l (kg m^{-3})	ρ_v (kg m^{-3})	ΔH_{vap} (J mol^{-1})
298.15	11.264	1606.4	0.8454[a]	36129
300.00	12.322	1602.3	0.9191[a]	36020
320.00	29.994	1556.9	2.097[a]	34931
340.00	64.350	1509.8	4.235[a]	33988
353.41	101.32	1477.0	6.416[a]	33420
360.00	124.80	1460.6	7.757[a]	33158
380.00	223.04	1408.7	14.27	29815
400.00	372.85	1353.4	23.28	28383
420.00	589.92	1293.5	37.13	26204
440.00	891.91	1227.2	57.62	23757
460.00	1298.9	1151.2	87.88	21004
480.00	1834.7	1058.4	134.6	17659
500.00	2530.6	928.1	217.5	12942
505.00	2734.8	881.4	251.8	11261
510.00	2953.4	819.9	300.3	9078.0
515.00	3189.1	713.4	392.5	5412.3
516.00	3238.9	667.5	435.0	3883.2
516.66	3273.2	550.5	550.5	0

[a] Ideal-gas density.
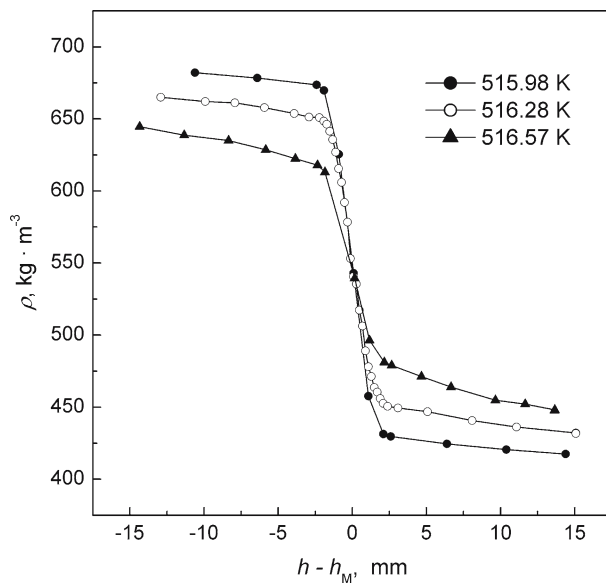
Fig. 6. Density of perfluorobenzene near the critical point as a function of the distance from the meniscus.

$$P_v(h) = g \int_h^{h_{max}} \rho_v(h)dh, \quad h \geqslant h_M \tag{12}$$

$$P_l(h) = g \int_h^{h_M} \rho_l(h)dh + P_v(h_M), \quad h < h_M \tag{13}$$

where P_v and P_l are the hydrostatic pressure in the vapor and liquid phases, $g = 9.8145 \, \text{m} \cdot \text{s}^{-2}$ is acceleration of gravity in Novosibirsk [15], and $h_{max} = 40 \, \text{mm}$ is the internal diameter of the experimental cell. The isothermal compressibility was calculated from the equation,

$$\chi_{v,l}^T(P, T_i) = \frac{1}{\rho_{v,l}(h, T_i)} \left(\frac{\partial \rho_{v,l}(h, T_i)}{\partial P(h, T_i)} \right)_{T_i} = -\frac{1}{g\rho_{v,l}^2(h, T_i)} \cdot \left(\frac{\partial \rho_{v,l}(h, T_i)}{\partial h} \right)_{T_i} \tag{14}$$

The approximated dependences $\rho_{v,l}(h)$ which have been obtained for the determination of the vapor and liquid densities on the saturation line were used as initial data. Figure 7 and Table III show the results of the calculations. The uncertainty in $\chi_{v,l}^T$ was 15–40%, and it is mainly determined by the error in $d\rho/dh$.
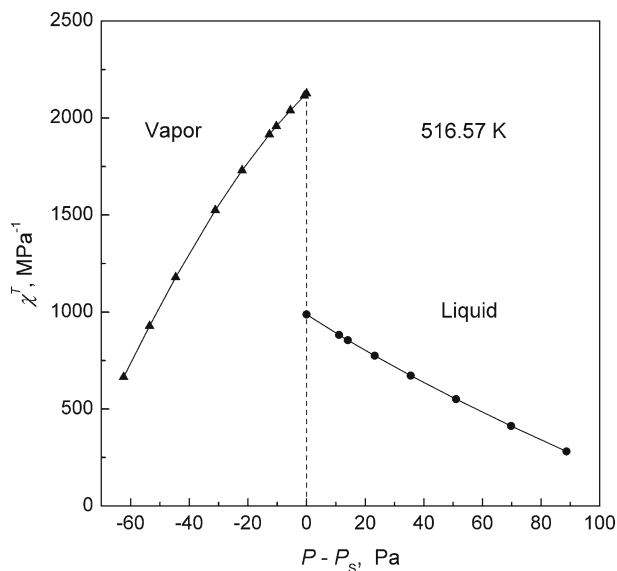

Fig. 7. Isothermal compressibility of perfluorobenzene as a function of the pressure at 516.57 K.

Table III. Estimated Isothermal Compressibility of Perfluorobenzene along the Coexistence Curve

T (K)	P_S (kPa)	χ_l^T (MPa^{-1})	χ_v^T (MPa^{-1})
515.98	3238.5	335	891
516.28	3253.7	657	1040
516.57	3268.6	985	2135

The asymptotic behavior of the isothermal compressibility on the liquid–vapor coexistence curve is described by [16]

$$\chi^T = A\varepsilon^{-\gamma} \tag{15}$$

where γ is the critical exponent for the compressibility. The treatment of Table III data gives the following values of the critical exponents:

$$\gamma_v = 0.45 \pm 0.10, \tag{16}$$
$$\gamma_l = 0.50 \pm 0.20 \tag{17}$$

(the uncertainties of both values denote the random errors of approximation). The γ_v and γ_l values coincide with each other, as the theory predicted. However, their absolute value is much less than the most reliable experimental results, $\gamma = 1.2$–1.3 [10]. It seems likely that it is due to more sharp changes of the phase's density in the immediate vicinity of the liquid–vapor interface, which is not taken into account for an extrapolation of $\rho_{l,v}(h)$ dependences to the meniscus. For a reliable determination of the critical exponent for the compressibility, it is necessary to handle all data with the help of an equation of state, which is carried out in the critical region.

4. CONCLUSION

The density of vapor and liquid perfluorobenzene along the liquid–vapor coexistence curve has been studied by a gamma-ray attenuation technique over the temperature range from 298.8 to 517.3 K. The purity of the samples used throughout the measurements was 99.67 mol%. The experimental uncertainties of the temperature and density measurements were estimated to be within ± 0.05 K and $\pm$ 1–1.5 kg$\cdot$m^{-3}, respectively. The critical temperature, critical density, critical exponent of the coexistence curve, temperature dependences of the liquid and vapor density along the saturation line were determined. On the basis of the results from

this study and literature data, the enthalpy of vaporization of perfluorobenzene was calculated. The height dependence of the density of the two-phase sample was investigated in relation to the temperature and time. These experiments made it possible to determine the isothermal compressibility of the liquid and vapor phases near the critical point.

ACKNOWLEDGMENTS

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