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COEXISTENCE CURVE FOR A LIQUID AND GAS NEAR THE CRITICAL POINT

M. Sh. GITERMAN and S. P. MALYSHENKO

All-union Institute of Physico-technical and Radiotechnical Measurements; Institute of High Temperatures, USSR Academy of Sciences

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The shape of the coexistence curve (ordering parameter as a function of temperature) is an important characteristic of critical phenomena and second-order phase transitions. An analysis of the experimental data shows that in the immediate vicinity of the transition point the cubic law is replaced by a quadratic one. Possible explanations of this behavior are discussed. The effect of the logarithmic singularity of the specific heat c_V on the shape of the coexistence curve is analyzed within the framework of the phenomenological theory. Formulas are deduced for the hydrostatic effect as a function of vessel height and degree of approach to the critical point. Its effect on the experimental coexistence curve is investigated.

A large number of physical quantities (c_p, c_V, $(\partial V/\partial T)_p$, $(\partial V/\partial p)_T$) possess a singularity at the critical point. An experimental investigation of the character of the singularities of these quantities is very important for the construction of a correct theory (microscopic or phenomenological) describing the properties of a liquid in the near-critical region. No less interesting is the question of the form of the coexistence curve near the critical point.

The classical theory, based on the expandability of the thermodynamic quantities in power series in the deviation of the temperature and of the specific volume ($t = (T - T_c)/T_c$, $v = (V - V_c)/V_c$), yields for the coexistence curve the law $(-t) \sim v^2$[1]. The microscopic theory (the Ising model) in the exactly-solved two-dimension problem gives for the coexistence curve the law $(-t) \sim v^8$, and approximate methods in the three-dimensional case yield a result close to $(-t) \sim |v|^3$[2]. There are quite a few experimental data describable, as a rule, by the Guggenheim empirical formula $(-t) \sim |v|^3$[3]. At the same time, certain results[4,5] point to the quadratic dependence $(-t) \sim v^2$.

We shall consider first the influence of the most important factors that determine the form of the coexistence curve, and then turn to a thorough analysis of the available experimental data.

1. LOGARITHMIC SINGULARITY OF THE SPECIFIC HEAT AND THE FORM OF THE COEXISTENCE CURVE

The phenomenological theory of critical phenomena[1] leads to a finite specific heat c_V at the critical point, thus contradicting the known experimental data.

A generalization of the phenomenological theory with allowance for a logarithmic singularity of c_V at the critical point, presented in[6], leads to the following form of the free energy:

$$F = F_{\text{reg}} + \alpha t^2 \ln[(t + \beta v^2)^2 + \gamma^2 v^4] + t^2 h(t/v^2), \tag{1}$$

where F_{reg} is determined by expanding the thermodynamic quantities in powers of t and v with allowance for the relation $(\partial p/\partial V)_{Tk} = (\partial^2 p/\partial V^2)_{Tk} = 0$, i.e.,

$$F_{\text{reg}} = \psi(t) - v\varphi(t) + \frac{atv^2}{2} + \frac{bv^4}{12} + \ldots. \tag{2}$$

The explicit form of the functions h, ψ, and φ is immaterial for what follows.

From (1) and (2) we can easily obtain an expression for the pressures p and chemical potentials μ. The equation of the coexistence curve is determined, as is well known, from the conditions

$$\mu_g(t, v) = \mu_l(t, v), \quad p_g(t, v) = p_l(t, v).$$

It turns out that the coexistence curve remains a quadratic parabola even when account is taken of the irregular terms in the free energy; the parameters of the parabola depend both on the regular (a, b) and the singular (α, β, γ) parts of the equation of state. To obtain the equation of the coexistence curve in the next higher approximation it is necessary to take into account the correction terms for the regular and singular parts of the thermodynamic quantities.

The influence of the correction terms in (2) on the form of the coexistence curve was discussed in a paper by one of the authors[7]. The terms of higher order in the pre-logarithmic factor of (1) are of the form $\eta t v^3 + \zeta v^5 + \xi t^2 v$[6]. Allowance for these terms is made in complete analogy with[7] and leads to the following form of the coexistence curve:

$$t = -\chi v^2 + \theta v^3 \ln v^2 + \ldots \tag{3}$$

On the other hand, if the singular addition (1) to the free energy is an even function of v, i.e., $\eta = \zeta = \xi = 0$, then the equation of the coexistence curve is

$$t = -\chi v^2 + \theta_1 v^3 + \ldots \tag{4}$$

The coefficients χ, θ, and θ_1 in (3) and (4) are expressed in terms of the parameters introduced above for the equation of state.

The expression for the singular addition to the free energy (1) is apparently confirmed experimentally[5,8], although it is still impossible to determine the coefficient γ. At the same time, a direct experimental solution of the problem of the higher-order terms in the pre-logarithmic factor in (1) calls for definite evaluations of the higher-order derivatives of the thermodynamic potential, for which the experimental data as a rule are not sufficiently accurate. However, this interesting question can possibly be solved (if the form of the coexistence curve is measured with sufficient accuracy) by an alternative choice between (3) and (4) in the analysis of the experimental data.

We note in conclusion that a few other variants of the phenomenological theory[9] also lead to the simultaneous existence of a logarithmic singularity in the specific heat and of a quadratic behavior of the coexistence curve. There exist also more general phenomenological theories (a review of which was presented by Griffiths[10]) admitting of both a quadratic and a cubic coexistence curve.

Thus, the phenomenological analysis (unlike the results of the computer calculations in the three-dimensional Ising model) shows that the logarithmic singularity of the specific heat does not at all call for a simultaneous cubic coexistence curve and in general it admits both $(-t) \sim v^2$ and $(-t) \sim |v|^3$.

2. INFLUENCE OF THE INHOMOGENEITY OF THE DENSITY OVER THE HEIGHT OF THE VESSEL ON THE EXPERIMENTALLY OBSERVED COEXISTENCE CURVE

The compressibility of a pure substance increases without limit near the critical point, and therefore the variation of the hydrostatic pressure with altitude in the vessel gives rise to a strong density inhomogeneity, which can greatly distort the experimental results.

In the absence of mixing, the characteristic parameter of the inhomogeneity of the density is the total height of the vessel H_m. The presence of mixing leads to a decrease of the dimensions of the inhomogeneity; this, however, does not eliminate the microscopic inhomogeneities at distances on the order of the correlation radius r_0[1)]. We shall henceforth take the characteristic parameters of the inhomogeneity to be the limiting values H_m and r_0, although in practice intermediate scales can also be realized.

In calculating the hydrostatic effect we shall use the equation of state in the form (2) without taking into account the irregular increments of the type (1). Allowance for the latter greatly complicates the calculation and at the same time apparently does not lead to a qualitative change of the conclusions. The logarithmic terms (1) are decisive for the derivatives of the free energy with respect to the temperature (specific heat, speed of sound, etc.) and affects to a much lesser degree the derivatives with respect to the volume (equation of state, compressibility, etc.).

The compressibility near the critical point is equal to

$$\frac{\partial p}{\partial \rho} = At + B\rho^2 + \ldots, \quad A = \left(\frac{\partial^2 p}{\partial \rho\, \partial t}\right)_c,$$
$$B = \frac{1}{2}\left(\frac{\partial^3 p}{\partial \rho^3}\right), \quad \rho = \frac{\mathcal{P} - \mathcal{P}_c}{\mathcal{P}_c}, \quad p = \frac{P - P_c}{P_c}. \tag{5}$$

By ρ and p we have denoted the relative deviations of the density $\mathcal{P}$ and the pressure P from their values at the critical point.

For the change of the pressure of the liquid with altitude we have

$$-dp = dh. \tag{6}$$

We have introduced here a dimensionless variable for the height of the vessel:

$$h = Hg\mathcal{P}_c / P_c, \quad h_m = H_m g\mathcal{P}_c / P_c \tag{7}$$

where the h axis is directed opposite to g, and the origin is chosen at the level where the density gradient is minimal[2)], so that $h < 0$ corresponds to a liquid and $h > 0$ to a gas.

Combining (5) and (6) we arrive (when t = const) to an equation that determines the dependence of the density on the altitude:

$$\rho^3 + \frac{3At}{B}\rho + \frac{3h}{B} = 0. \tag{8}$$

In the limiting case h = 0 we obtain from (8) the densities of the coexisting phases at the interface, $\rho_{1,2} = \pm(-3At/B)^{1/2}$, and for t = 0 we get the density distribution over the height at $T = T_c$: $\rho = -(3h/B)^{1/3}$; both results are well known[1,11].

Experiment yields the average density

$$\bar{\rho} = \frac{1}{h_m}\int_0^{h_m} \rho(h)\, dh, \tag{9}$$

the density of the liquid being obtained when $h_m < 0$ and that of the gas when $h_m > 0$. Thus, the solution of the cubic equation (8) and subsequent calculation of $\bar{\rho}$ by means of (9) makes it possible to determine the corrections to the experimentally observed coexistence curve $\bar{\rho}(t)$ due to the finite height of the vessel, and also the hydrostatic effect $\bar{\rho}(h_m)$ at $T \neq T_c$.

When $t \geq 0$ the equation has a single root, and when $t < 0$ the number of roots is determined by the sign of the discriminant, namely, for

$$|h| > |h_0| = \frac{2B}{3}\left(-\frac{At}{B}\right)^{3/2} \tag{10}$$

the equation has a single unique root

$$\rho = \left(-\frac{3h}{2B}\right)^{1/3}\left\{\left[1 - \left(1 - \frac{h_0^2}{h^2}\right)^{1/2}\right]^{1/3} + \left[1 + \left(1 - \frac{h_0^2}{h^2}\right)^{1/2}\right]^{1/3}\right\}. \tag{11}$$

If the inequality opposite to (10) is satisfied, then (8) has three real roots, of which one corresponds to the stable state $(\partial p/\partial \rho)_t < 0$, and the other to a metastable state, while the root corresponding to the stable state is equal to

$$\rho_{1,2} = -2r\cos\frac{\varphi}{3},$$
$$r = \begin{cases} +(-At/B)^{1/2} & \text{if} \quad h > 0 \\ -(-At/B)^{1/2} & \text{if} \quad h < 0 \end{cases}, \qquad \cos\varphi = \frac{h}{h_0}. \tag{12}$$

When $H = h_0$ the two roots of (8) coincide, $\rho = \pm(-At/B)^{1/2}$, defining the spinodal points.

For $|h_m| \ll |h_0|$ or $|t| > |t_0| = (B/A) \times (3|h_m|2B)^{2/3}$, substituting (12) in (9) and integrating accurate to first-order terms in $|h_m|/|h_0|$, we have

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[1)] This interesting "microhydrostatic" effect was pointed out to us by Leo Kadanoff. According to his estimates $t_c \sim 10^{-(5\pm1)}$ for CO_2 (see below).

[2)] Thus, in a two-phase system the measurement is from the meniscus, and for the "liquid" (gaseous) branch of the coexistence curve—from the upper (lower) level.

$$\bar{\rho} = \pm\left(-\frac{3At}{B}\right)\left(1 + \frac{1}{6\sqrt{3}}\frac{h_m}{h_0} + \ldots\right) = \pm\left(-\frac{3At}{B}\right)^{1/2} + \frac{h_m}{4At} + \ldots, \qquad |h_m| \ll |h_0|. \tag{13}$$

For $|h_m| \gg |h_0| = (2/3)B(-At/B)^{3/2}$ it is necessary to break up the integral in (9) into two regions: in the region $(0, h_0)$ it is necessary to use (12), and in (h_0, h_m) it is necessary to use (11). We finally obtain, confining ourselves to first-order terms in $|h_0|/|h_m|$,

$$\bar{\rho} = \frac{3}{4}\left(-\frac{3h_m}{B}\right)^{1/3}\left[1 + 2^{1/3}\left(\frac{h_0}{h_m}\right)^{2/3} + \ldots\right] = \frac{3}{4}\left(-\frac{3h_m}{B}\right)^{1/3} + \frac{3At}{2(3h_mB^2)^{1/3}} - \ldots, \qquad |h_m| \gg |h_0|. \tag{14}$$

We proceed to an analysis of the fundamental formulas (13) and (14). From (13) we see that the "classical" result $\bar{\rho}_{1,2} = \pm(-3At/B)^{1/2}$ is obtained only in a fully homogeneous liquid (inhomogeneity parameter $h_m = 0$). In measuring the form of the coexistence curve $\bar{\rho}(t)$ for a given value of h_m (e.g., in the absence of mixing in a vessel of height H_m), the "classical" result remains in force only for temperatures $|t| \gg |t_0|$, and the correction due to the inhomogeneity is equal to $h_m/4At$. In the opposite limiting case $|t| \ll |t_0|$, formula (14) holds true and the coexistence curve will take the form $\rho = \text{const} + \text{const} \cdot t$. Such a result (in the absence of mixing) was actually observed in[12].

In measuring the hydrostatic effect $\bar{\rho}(h_m)$ for a given proximity to the critical point, the well known result $\rho \propto (-3h_m/B)^{1/3}$ remains in force only if $|h_m| \gg |h_0|$. On the other hand, if $|h_m| \ll |h_0|$, then the $\bar{\rho}(h_m)$ dependence, which determines the size of the flat section on the isoterms (see[11]), will be entirely different: $\bar{\rho} = \text{const} + \text{const} \cdot h_m$. For numerical estimates it is necessary to know the derivatives $A = (\partial^2 p/\partial\rho\partial t)_c$ and $B = (1/2)(\partial^3 p/\partial\rho^3)_c$ at the critical point. An estimate of B was obtained by Voronel'[13] from different experimental data for several substances. His result (in dimensionless variables) is $B \approx 0.6 \pm 0.2$.

Let us estimate A. To this end we can use data on the jump of the specific heat c_V on going through the coexistence curve[5], on the scattering of light (in CO_2[14] and Xe[15]), on p-V-T measurements (data reduction for different substances[16]), and on acoustic measurements[17]. These and similar investigations give close results[3]: A equals 6 ± 2[5], 6 ± 1[14], 3 ± 2[15], 4.7[16], and 6 ± 1[17].

For further estimates we assume $A = 6$ and $B = 0.6$. Using these results, and also typical values of the critical parameters ($P_c = 50$ atm, $P_c = 0.5\ \text{g/cm}^3$), we get

$$h_m \approx 10^{-5} H_m, \qquad h_0 \approx 6t^{3/2}, \qquad |t_0| \approx 9 \cdot 10^{-5} H_m^{2/3}. \tag{15}$$

It is assumed here that the inhomogeneity parameter H_m is expressed in centimeters. All the estimates can be readily obtained from (15). Thus, at an inhomogeneity parameter $H_m = 10$ cm (e.g., a non-miscible liquid situated in a vessel 10 cm high) $h_m \approx 10^{-4}$ and the condition $h_m = h_0$ corresponds to $|t_0| = 3 \times 10^{-4}$ (for $T_c = 300°K$ this yields $T_c - T = 0.1°K$), i.e., formula (13) is valid for $|t| \gg 3 \times 10^{-4}$, and (14) is valid for $|t| \ll 3 \times 10^{-4}$.

A special analysis must be made of the "microhydrostatic" effect, since the correlation radius increases on approaching the critical point (apparently like[18] $r_0 = a_0|t|^{-2/3}$ in the dimensionless variables (7) $a_0 = 10^{-10}$). For such small inhomogeneity parameters, for all really attainable approximations to the critical point $|h_m| < |h_0|$, formula (13) holds and

$$\bar{\rho} = \pm\left(-\frac{3At}{B}\right)^{1/2} \mp \frac{a_0}{4A}(-t)^{-5/3}. \tag{16}$$

With decreasing $|t|$, the second term of (16) increases and the first decreases. The increment becomes of the order of the main term when $|t_c| \approx 10^{-(6\pm1)}$. This estimate shows the maximum "reasonable closeness" to the critical point (even for good mixing) - for temperatures closer to critical, the decisive factor is the influence of the inhomogeneity of the density at a distance on the order of the correlation radius.

We have thus obtained quantitative estimates for the usual requirements of "sufficient smallness" of the height of the vessel in measurement of the coexistence curve and the "sufficient closeness" to the critical in measurement of the hydrostatic effect. These estimates, the presence of the "microhydrostatic" effect, and the clarification of the role of the mixing (the latter calling for a special investigation) must be borne in mind in the analysis of the corresponding experiments.

At the same time, in order to find the parameters of the equation of state it is of interest to measure the coexistence curve in a vessel with a height known to be "large" (where $\bar{\rho} = \text{const} + \text{const} \cdot t$, and not $\sim \sqrt{|t|}$), and the hydrostatic effect should be measured sufficiently "far" from the critical point (where $\rho = \text{const} + \text{const} \cdot h_m$, and not $\sim h_m^{1/3}$).

3. ANALYSIS OF THE EXPERIMENTAL DATA

We deemed it necessary to analyze all the available experimental data, principally from the point of view of their proximity to the critical point. It turned out that the greatest proximity to the critical point is attained in experiments with xenon[19], ethylene (C_2H_4)[12], sulfur tetrachloride (SF_6)[20,23], chlorine (Cl_2)[21], and helium[22].

The experimental data for these substances in a log-log scale ($\log|t|$, $\log|\rho|$) are shown in Figs. 1–3. In order not to make the scale of the figures too small, we had to leave out the points for $|\rho| > 10^{-1}$ and $|t| > 10^{-3}$.

When $|\rho| > 10^{-1}$ and $|t| > 10^{-3}$ the experimental points fit the plot of $|\rho| \sim |t|^n$ with $n = 1/3$, the continuation of which in the figures are the straight lines 1. We see that on approaching the critical point, starting with $|t| \lesssim 10^{-3}$, a systematic deviation from the $|\rho| \sim |t|^{1/3}$ law is observed, and the degree n changes smoothly and assumes the value $n \approx 1/2$ near the critical point (straight lines 2).

Figure 1 does not show the two points closest to critical for Xe and two points for SF_6, which agree with the relation $|\rho| \sim |t|^{1/2}$, in view of the fact that the error of $|t|$ becomes too large and the points were

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[3] Incidentally, some investigations yield lower values of A. However, an analysis of this question is beyond the scope of the article.

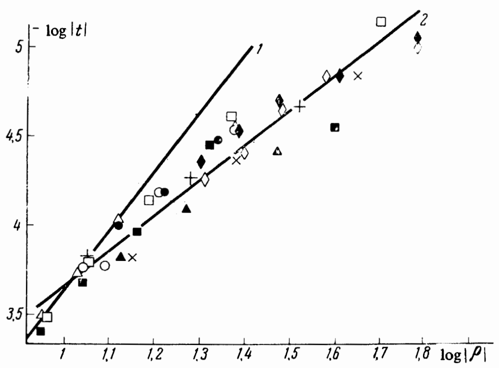

FIG. 1. Coexistence curve for C_2H_4, Xe, and SF_6 in the immediate vicinity of the critical point. Line 1 corresponds to $(-t) \sim |\rho|^3$, and line 2 to $(-t) \sim \rho^2$; experimental points: C_2H_4[12], ●–gas, ○–liquid at H_m = 15 cm, ×–gas, +–liquid at H_m = 6 cm; Xe[19], ■–gas, □–liquid; Xe[12], ▲–gas, △–liquid; SF_6[23], ◆–gas, ◇–liquid.

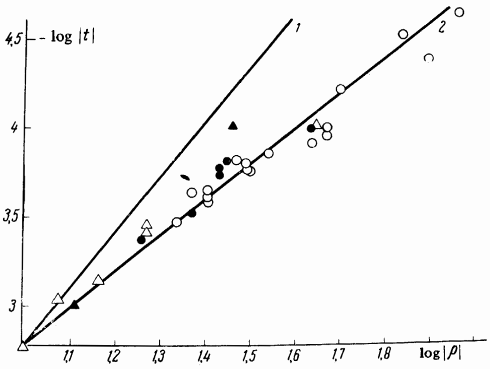

FIG. 2. Coexistence curve of Cl_2 and SF_6 in the immediate vicinity of the critical point. Line 1 corresponds to $(-t) \sim |\rho|^3$ and line 2 to $(-t) \sim \rho^2$; experimental points: Cl_2[21], ●–gas, ○–liquid; SF_6[20], ▲–gas, △–liquid.

obtained at the borderline of the measurement accuracy; in addition, at these orders of $|t|$ the hydrostatic effect considered in Sec. 2 may exert an influence.

Figures 1 and 2 show clearly that when $|\rho| < 10^{-1}$ the experimental points for Xe, Cl_2, SF_6, and C_2H_4 agree well with the relation $(-t) \sim \rho^2$ and cannot be represented in any way by a cubic law.

The coexistence curve of helium up to $|t| \sim 4 \times 10^{-5}$ and $|\rho| \sim 1.4 \times 10^{-2}$ was investigated in[22], whose authors represented their data with $|t|$ and $|\rho|^{1/3}$ as coordinates and state that the coexistence curve is a cubic parabola. However, from the data tabulated in[22], which are plotted in our Fig. 3, we see that starting with $|\rho| \sim 10^{-1}$, the points deviate systematically from the $(-t) \sim |\rho|^3$ law, just as in the case of Xe, Cl_2, SF_6, and C_2H_4, and confirm more readily a quadratic than a cubic dependence. Incidentally, the scatter of the experimental points is larger for He than for the other gases.

Thus, the coexistence curve near the critical point is of the form[4]

$$t = -\gamma\rho^2 + \delta\rho^3 + \dots \qquad (17)$$

The liquid and gas branches of Fig. 1 do not coincide in general, but on approaching $t = \rho = 0$ they come together and the plot of $|\rho|$ against $|t|$ is symmetrical near the critical point. We note that the coordinates $\log|t|$ and $\log|\rho|$ are more sensitive to the $t(\rho)$ dependence when $t \to 0$ and $\rho \to 0$ than the coordinates of the type $|\rho|^n$ and $|t|$ or $|t|^N$ and $|\rho|$, for which the points near $t = \rho = 0$ fit equally well the plots of $|\rho| \sim |t|^{1/2}$ or $|\rho| \sim |t|^{1/3}$.

Thus, in the interval $|\rho| \sim 10^{-2} - 10^{-1}$ the experimental data for all the substances under consideration fit the $|t| \sim \rho^2$ dependence with the same accuracy with which the data for $|\rho| > 10^{-1}$ agree with $|t| \sim |\rho|^3$ dependence. Allowing for a scatter on the order of the experimental accuracy, the data for different substances can be represented by the first term of Eq. (17) in the interval $(t_{\min}, \rho_{\min} - t_1, \rho_1)$ and two terms in the interval $(t_{\min}, \rho_{\min} - t_2, \rho_2)$. With increasing distance from the critical point (up to $|\rho| \sim 10^{-1}$) the experimental points follow a steeper curve. But in this interval ρ changes already by one order of magnitude ($|\rho| \sim 10^{-1}$), so that terms of higher order in ρ must be taken into account in the power-law expansions (see (17)).

The table lists the coefficients of (17) determined from the experimental data: in the region from $t_{\min}$, $\rho_{\min}$ to t_1, ρ_1) only the first term of the right side of (17) can be retained; when $|\rho| > 10^{-1}$ it is necessary to take into account the second term of (17). At larger $|\rho|$ or $|t|$ it may be necessary to take into account the succeeding terms in (17).

The coefficients δ are already strongly affected by the asymmetry of the curve, so that the value of δ is given separately for the liquid and for the gas, and this coefficient cannot be determined for SF_6 and Cl_2, since almost all the points fall on the quadratic plot. The accuracy is not sufficient for an experimental choice between (3) and (4) (only a clear-cut deviation from quadratic behavior is observed), and special investigations are necessary for a convincing determination of the character of these deviations. The table does not give the values of the coefficients γ and δ for He, in view of the small number of points in the direct vicinity of the critical point.

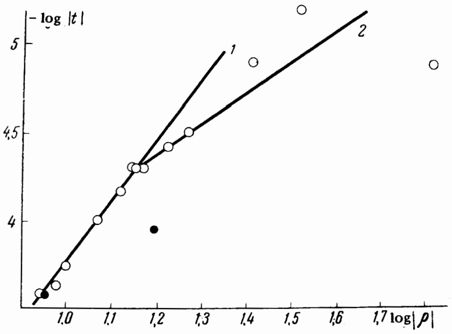

FIG. 3. Coexistence curve of helium in the immediate vicinity of the critical point. Line 1 corresponds to $(-t) \sim |\rho|^3$ and line 2 to $(-t) \sim \rho^2$. Experimental points: [22] ○–gas, ●–liquid.

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[4] Owing to the lack of experimental data, we decided not to introduce the deviations from the integers in the exponents.

Substance	Experimental data	$\gamma\cdot 10^2$	$\delta\cdot 10^2$, liquid	$\delta\cdot 10$, gas	$\lvert t_1\rvert$	$\lvert \rho_1\rvert$	$\lvert t_2\rvert$	$\lvert \rho_2\rvert$
Xe[19]	$\lvert t\rvert_{min}=10^{-5}$ $\lvert \rho\rvert_{min}=2\cdot 10^{-2}$	1.65 ± 0.15	4.4 ± 0.4	1 ± 0.2	$5\cdot 10^{-5}$	$5\cdot 10^{-2}$	$2\cdot 10^{-4}$	10^{-1}
C_2H_4[12]	$\lvert t\rvert_{min}=2\cdot 10^{-5}$ $\lvert \rho\rvert_{min}=3\cdot 10^{-2}$	1.65 ± 0.15	4.4 ± 0.4	4.8 ± 0.2	$5\cdot 10^{-5}$	$5\cdot 10^{-2}$	$2\cdot 10^{-4}$	10^{-1}
SF_6[23]	$\lvert t\rvert_{min}=4.7\cdot 10^{-6}$ $\lvert \rho\rvert_{min}=8.4\cdot 10^{-3}$	1.65 ± 0.15			$5\cdot 10^{-5}$	$5\cdot 10^{-2}$	—	—
SF_6[20]	$\lvert t\rvert_{min}=10^{-4}$ $\lvert \rho\rvert_{min}=10^{-2}$	18 ± 2	—	—	$5\cdot 10^{-4}$	$5\cdot 10^{-2}$	—	—
Cl_2[21]	$\lvert t\rvert_{min}=4.8\cdot 10^{-6}$ $\lvert \rho\rvert_{min}=5\cdot 10^{-3}$	18 ± 2	—	—	$5\cdot 10^{-4}$	$5\cdot 10^{-2}$	—	—

It is seen from Figs. 1 and 2 and from the table that the data for SF_6, obtained by different investigators[20] and[23], although each favoring a quadratic coexistence curve, do not agree with each other. The causes of this disagreement are not quite clear. Our investigation has confirmed that consideration of only points that are far from critical or figure to take into account the experimental errors, which increase with increasing proximity to the critical point, can lead to relations of the type $-t \sim |\rho|^3$. It is possible, however, on the basis of the data indicated above, that sufficiently close to the critical point the coexistence curve is second-degree parabola. This gives rise to a discrepancy between the experimental result and the data of the approximate calculations in the three-dimensional Ising model, which give $(-t) \sim |\rho|^3$. In our opinion there are three possible ways of overcoming this contradiction.

First, it remains unclear which interval (in terms of $|t|$ and $|\rho|$) should be regarded as "so close" to the critical point that" a singularity appears in it," i.e., a deviation from the predictions of the ordinary theory is observed[1]. Theoretical estimates were made by Ginzburg[24] (a region in which the fluctuation energy is of the order of the equilibrium energy) and by Vaks and Larkin[25], who studied the deviations from classical theory for substances with long-range forces. It follows from these investigations that the temperature intervals in which the singularity appears are practically the same for the specific heat and for the coexistence curve. It is therefore extremely interesting to compare sufficiently accurate measurements of the specific heat and of the coexistence curve for the same substance in the direct vicinity of the critical point 5). It is possible that the singularities in the coexistence curve arise closer to the critical point than those of the specific heat, and this interval has not yet been attained experimentally. But the hydrostatic effect (see Sec. 2) makes it impossible to come too close to the critical point, and it is therefore not excluded that the interval of the singularity of the coexistence curve is not accessible to experiment at all 6).

Another possibility of overcoming the foregoing contradiction lies in the fact that actually the temperature interval in which "the singularity appears" in the coexistence curve is located relatively far from the critical point ($|t| > 10^{-3}$; $|\rho| \geq 10^{-1}$) where, as already mentioned, the experimental points are well described by the cubic law, and a "classical" behavior sets in again closer to the critical point, for example, as a result of impurities 7). The situation is thus the opposite of the expected one: as $T \to T_c$ the cubic law is replaced by a quadratic one for the coexistence curve, and not vice-versa.

The role of the impurities in the phase transitions and critical phenomena has not been thoroughly investigated. It is possible[28] that the impurity concentration c enters in the irregular part of the free energy, in the form $t^2 \ln(|t| + c)$. Then the impurities have no effect up to $|t| > c$, and their influence becomes appreciable only sufficiently close to the critical point. This question calls for a special investigation.

Finally, the third possibility is more radical and postulates the inapplicability of the Ising model (at least in the presently known approximate calculation) to critical phenomena. A discrepancy between the Ising model and experiment has already been observed - calculation predicts that the pre-logarithmic factor in c_V differs by an approximate factor of 3 when the critical point is approached from the homogeneous and heterogeneous regions, whereas experiments[8] show that the plots of c_V against $\ln|t|$ have the same slopes on both sides of T_c.

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5) We call attention to a paper by Strukov, Taraskin, and Koptsik[26], who investigated the ferroelectric transition in triglycinfluoroberyllate. In the interval $|t| \lesssim 6 \times 10^{-3}$ they observed a clear-cut logarithmic variation of the specific heat, whereas the dependence of the spontaneous polarization on the degree of proximity to the transition point remained "classical." Of course, the ferroelectric transition has a number of unique features and cannot be set in direct correspondence with the critical point of a liquid.

6) There is only one experimental investigation (Lorentzen[27]) of the coexistence curve of CO_2 up to $|t| \sim 3 \times 10^{-6}$ and $|\rho| \sim 10^{-2}$, where it turned out that $(-t) \sim |\rho|^3$. In view of the fact that the results of[27] are plotted only in coordinates $|\rho|$ and $|t|^{1/3}$, and the experimental points are not presented, it is impossible to analyze the experimental data in the manner used above. However, if the conclusion of[27] is correct, then it is possible that the "singularity interval" was indeed attained in this investigation. It is interesting that with increasing distance from the critical point ($|t| > 2 \times 10^{-5}$), two points on the plot deviate towards a decrease in the degree of the $(-t) \sim |\rho|^n$ curve; unfortunately, no measurements were made in that investigation at larger values of ρ and t.

7) This idea belongs to G. V. Ryazanov.

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