

The laboratory equipment simulating a so-called no-flow system provided for the liquid flow to intersect a magnetic field in a high-temperature reactor. The liquid was heavy fuel oil 40. The reactors were steel vessels set up in pairs in an oven, where the liquid was kept at 753-773°K for eight hours. The paired reactors provided identical thermal conditions for the simultaneous flows of liquid, one of which was treated with the magnetic field. The amount of coke was determined from the weight change. The field strength varied from 100 to 1000 Oe. From the magnetized raw material the yield of coke increased by comparison with the untreated liquid (up to 40% in individual runs).

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CRITICAL AMPLITUDES OF PURE SUBSTANCES

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Consequences of theoretical models for the critical amplitudes A, B, Γ , D are considered and calculated values of critical amplitudes for pure substances are presented for the range $Z_{cr} = p_{cr}v_{cr}/RT_{cr} = 0.22-0.29$, as obtained by the proposed expressions.

Near the critical point the behavior of thermodynamic functions of pure substances on the fundamental curves is defined by asymptotic exponential functions:

$$C_v/(RZ_{cr}) = A|t|^{-\alpha} \quad \text{on the critical isochor;}$$

$$\Delta\rho = B(-t)^\beta \quad \text{on the boundary curve;}$$

$$\left(\frac{\partial\omega}{\partial\pi}\right)_\tau = \Gamma|t|^{-\gamma} \quad \text{on the critical isochor;}$$

$$|\Delta\rho| = D|\Delta\rho|^\delta \quad \text{on the critical isotherm.}$$

Here $\tau = t + 1 = T/T_{cr}$, $\pi = \Delta\rho + 1 = p/p_{cr}$, $\omega = \Delta\rho + 1 = \rho/\rho_{cr}$, $Z_{cr} = p_{cr}v_{cr}/(RT_{cr})$.

The modern theory of critical phenomena predicts that the critical exponents α , β , γ , δ do not depend on the nature of the substance, but are universal constants [1]:

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TABLE 1. Critical Amplitudes of Eq. (13) vs Compressibility Coefficient at Critical Point

z_{cr}	n	A_1	B	Γ	D
0,22	1,5325	32,425	2,983	0,1372	0,8191
0,23	1,5607	29,783	2,891	0,1403	0,8528
0,24	1,5892	27,464	2,805	0,1432	0,8879
0,25	1,6180	25,416	2,723	0,1459	0,9242
0,26	1,6471	23,600	2,647	0,1484	0,9618
0,27	1,6765	21,980	2,574	0,1508	1,0008
0,28	1,7061	20,531	2,506	0,1529	1,0412
0,29	1,7360	19,227	2,441	0,1550	1,0830
0,375	2	12	2	0,1667	1,5

TABLE 2. Critical Amplitudes of Lattice Gas Model at $\alpha = 1/8$; $\beta = 5/16$; $\gamma = 5/4$; $\delta = 5$

Lattice	z_{cr}	A	B	Γ	D	$A\Gamma/B^2$	$D\Gamma B^{\delta-1}$
Diamond	0,1869	25,04	1,666	0,05584	4,173	0,5037	1,795
SC	0,2257	20,13	1,569	0,05973	4,741	0,4885	1,716
BCC	0,2488	17,78	1,506	0,06138	5,305	0,4812	1,675
FCC	0,2585	16,85	1,487	0,06275	5,532	0,4782	1,697

$$\begin{aligned} \alpha &= 0,112 \pm 0,002; & \beta &= 0,324 \pm 0,002; \\ \gamma &= 1,240 \pm 0,002; & \delta &= 4,83 \pm 0,03. \end{aligned} \quad (1)$$

The critical amplitudes A , B , Γ , D do depend on the nature of the substance, but they form certain complexes which are universal constants. Analysis of the equations of thermodynamics gives the following expressions for the universal complexes of the critical amplitudes [2]:

$$A_1\Gamma'/B^2 = \beta^2, \quad (2)$$

$$D\Gamma'B^{\delta-1} \geq \frac{1}{\delta} \left(1 + \frac{1-\alpha-\beta}{\gamma} \right), \quad (3)$$

where A_1 and Γ' are critical amplitudes for the shift in isochoric heat capacity and the derivative $(\partial\omega/\partial\pi)_T$ on the boundary curve.

The universality of this set of critical amplitude complexes is also indicated by various empirical equations of state for the critical region. In particular, the linear model of the parametric equation of state

$$(\mu - \mu_a)/(\rho_{cr} v_{cr}) = ar\beta^\delta \theta(1 - \theta^2), \quad t = r(1 - b^2\theta^2); \quad \Delta\rho = kr^\beta \theta, \quad (4)$$

where μ_a is the analytic portion of the chemical potential,

$$b^2 = \frac{\gamma - 2\beta}{\gamma(1 - 2\beta)}; \quad (5)$$

r and θ are parametric variables; α and k are individual constants of the substance determined from the values of its critical amplitudes, gives the following expressions for the universal complexes of critical amplitudes:

$$\frac{A\Gamma}{B^2} = \frac{\gamma(\gamma - 1)}{2\alpha} \frac{(b^2 - 1)^{2\beta}}{b^2}, \quad (6)$$

$$D\Gamma B^{\delta-1} = b^{\delta-3}/(b^2 - 1)^{\gamma-1}, \quad (7)$$

$$\frac{\Gamma}{\Gamma'} = \frac{2(\gamma-1)}{(1-2\beta)(b^2-1)^\gamma}; \quad (8)$$

$$\frac{A'}{A} = \left(\frac{1-2\beta}{\gamma-1}\right)^2 (b^2-1)^\alpha; \quad (9)$$

$$\frac{A_1}{A} = \frac{\alpha(\gamma-2\beta)}{(\gamma-1)^2} (b^2-1)^\alpha. \quad (10)$$

Here A' is the critical amplitude of the heat capacity C_V on the critical isochor in the two-phase region.

It should be noted that the values of the critical amplitude complexes Eqs. (6)-(10) depend not only on the critical exponents, but also to some degree on the form of the asymptotic equation of state. Thus, for a cubic model of the parametric equation of state

$$(\mu - \mu_a)/(p_{cr} v_{cr}) = a_1 r^{\beta\delta} \theta (1 - \theta^2), \quad t = r(1 - d^2 \theta^2); \quad \Delta\rho = k_1 r^\beta \theta (1 + c\theta^2), \quad (11)$$

where

$$d^2 = \frac{3}{3-2\beta}; \quad c = \frac{2\beta\delta-3}{3-2\beta}, \quad (12)$$

the values of the complexes $D\Gamma B^{\delta-1}$ and Γ/Γ' at the theoretical values of the critical exponents of Eq. (1) are elevated above the values predicted by the linear model of Eq. (4) by 0.5 and 0.9%, respectively.

Since the differences between the values of the critical amplitude complexes predicted by the empirical equations of state are significantly less than the uncertainty with which they can be determined experimentally, Eqs. (6)-(10) together with known values of two critical amplitudes can be used to determine the values of the remaining amplitudes while introducing an additional uncertainty of ~1%.

The character of the dependence of critical amplitudes on the nature of the substance involved is also of interest. As the parameter defining the nature of the substance, we will use the value of the compressibility coefficient at the critical point $Z_{cr} = p_{cr} v_{cr} / RT_{cr}$.

We will consider a Van der Waals equation of state in which the correction to pressure for intermolecular attraction forces is written in the general form

$$\left(\pi + \frac{a}{\varphi^n}\right) (\varphi - b) = \tau / Z_{cr}, \quad (13)$$

where $\varphi = v/v_{cr}$. The asymptotic behavior of Eq. (13), like the Van der Waals equation, is defined by the critical exponents $\alpha = 0$, $\beta = 1/2$, $\gamma = 1$, $\delta = 3$. The parameters of Eq. (13) and the critical amplitudes of the basic thermodynamic functions are related to the exponent n by the following expressions:

$$\left. \begin{aligned} a &= \frac{n+1}{n-1}; & b &= \frac{n-1}{n+1}; & Z_{cr} &= \frac{n^2-1}{4n}; \\ A_1 &= \frac{6n}{(n-1)^2}; & B &= \frac{2\sqrt{3}}{\sqrt{n^2-1}}; & \Gamma &= \frac{n-1}{n(n+1)}; \\ D &= \frac{1}{12} n(n+1)^2. \end{aligned} \right\} \quad (14)$$

For clarity we present the dependence of the critical amplitudes of Eq. (13) on Z_{cr} in Table 1.

Table 2 shows values of Z_{cr} and critical amplitudes for four lattices (diamond, simple cubic (sc), body-centered cubic (bcc), face-centered cubic (fcc)) of the lattice gas model. Values of the critical amplitudes for the lattice gas (lg) model were recalculated from values of the critical amplitudes for the Ising magnetic model (m) with the following expressions:

$$A_{lg} = A_m \frac{4}{Z_{cr}}; \quad B_{lg} = B_m; \quad \Gamma_{lg} = \Gamma_m \frac{Z_{cr}}{4}; \quad D_{lg} = D_m \frac{2}{Z_{cr}}. \quad (15)$$

TABLE 3. Experimental Estimates of Parameters of the Asymptotic Dependence of Specific Heat C_V on the Critical Isochor at $T \geq T_{cr}$

Substance	Z_{cr}	α	A	Source
H ₂ O*	0,229	0,11	26,7	[8]
CO ₂	0,274	0,124±0,014	20,80±4,74	[9]
C ₂ H ₆	0,2795	0,11	21,81	[10]
Ar	0,290	0,115	17,87±3,75	[11]

*Parameters of asymptotic function obtained from data on speed of sound.

TABLE 4. Values of Critical Amplitudes of Real Substances Calculated with Use of Theoretical Critical Exponents, Eq. (1)

Z_{cr}	A	B	Γ	D
0,22	36,1	1,950	0,0528	2,48
0,23	33,5	1,894	0,0537	2,74
0,24	31,0	1,834	0,0545	3,05
0,25	28,4	1,769	0,0554	3,45
0,26	25,8	1,698	0,0562	3,97
0,27	23,1	1,620	0,0570	4,69
0,28	20,3	1,529	0,0579	5,76
0,29	17,2	1,420	0,0587	7,54

In [3-6] values of the critical amplitudes for the three-dimensional Ising model were obtained for the following critical exponent values: $\alpha = 1/8$; $\beta = 5/16$; $\gamma = 5/4$; $\delta = 5$. These correspond to critical amplitude complex values in Eqs. (6), (7) of $A\Gamma/B^2 = 0.4728$ and $D\Gamma B^{\delta-1} = 1.7547$.

As is evident from Table 2, the values of the universal complexes predicted by the linear model of the parametric equation of state agree well with values obtained by the lattice gas model.

Thus, for both the Van der Waals gas and the lattice gas the character of the dependence of critical amplitudes on the nature of the substance is identical: the critical amplitudes A and B are decreasing functions of Z_{cr} , while the critical amplitudes Γ and D are increasing functions of Z_{cr} . The critical amplitude A changes most intensely. The weakest dependence is $\Gamma(Z_{cr})$ - for a change in Z_{cr} of 0.07 the critical amplitude Γ changes only 10% (Table 2).

The scattering of experimentally determined values of the critical exponents is quite large, which hinders study of the dependence of critical amplitudes upon nature of the substance involved. The experimental estimates which come closest to theoretical values are for the critical exponent of isochoric specific heat $\alpha = 0.11 \pm 0.01$ [7]. As is evident from Table 3, the qualitative form of the function $A(Z_{cr})$ for real substances also agrees with the predictions of the theoretical models.

The majority of experimental estimates of the critical exponent β are above the theoretical value. However, with consideration of correction terms in the asymptotic function the use of empirical values of the critical exponent for description of data on orthobaric densities provides no advantages as compared to use of the fixed theoretical value of the critical exponent β [12, 13]. On the basis of an analysis of data for 22 materials [13] we obtained function $B(Z_{cr})$ at $\beta = 0.324$ in the region $Z_{cr} = 0.227-0.307$:

$$B(Z_{cr}) = 1 + 3,2213 \sqrt{0,307 - Z_{cr}} \quad (16)$$

Precision studies of the isothermal compressibility of xenon [14] also indicate that use of a fixed value of the critical index $\gamma = 1.240 \pm 0.002$ is to be preferred for describing experimental data. Use of universal values of the critical exponents permits a more detailed study of the dependence of critical amplitudes on the nature of the substance.

Reliable determination of the functions $A(Z_{cr})$ and $\Gamma(Z_{cr})$ from analysis of experimental data is difficult, since the scattering in values of A and Γ for one and the same substance at identical values of the critical exponents reaches 20%.

The theoretical models predict that the critical amplitude Γ will depend weakly on Z_{cr} so that in a first approximation the function $\Gamma(Z_{cr})$ can be considered linear. For its determination we will use one reference value of Γ and the theoretically predicted slope of the function $\Gamma(Z_{cr})$ in the interval $Z_{cr} = 0.22-0.29$. If we make use of the functions $B(Z_{cr})$ and $\Gamma(Z_{cr})$ we can calculate the critical amplitudes A and D from values of the universal critical amplitude complexes, Eqs. (6), (7). For the theoretical critical exponents of Eq. (1) these complexes have the following values:

$$A\Gamma/B^2 = 0,5019; D\Gamma B^{8-1} = 1,6923. \quad (17)$$

As a reference value we will use the critical amplitude of isothermal compressibility of xenon ($Z_{cr} = 0.286$) $\Gamma = 0.0584 \pm 0.0009$, obtained at $\gamma = 1.240 \pm 0.002$ [14]. In this case the function $\Gamma(Z_{cr})$ has the form

$$\Gamma(Z_{cr}) = 0,0345 + 0,0834 Z_{cr}. \quad (18)$$

An additional confirmation of the reliability of the reference value of Γ used is its good agreement with experimental evaluations of the critical amplitude A of ethane and argon [10].

Values of the critical amplitudes A , B , Γ , D calculated with Eqs. (16), (18) and from the complexes of Eq. (17) are presented in Table 4. These functions can be used as a first approximation in developing nonanalytic equations of state and for description of the critical region of little studied substances.

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