EQUATIONS OF STATE AND THERMODYNAMIC PROPERTIES OF CARBON DIOXIDE
AND ARGON IN THE CRITICAL REGION

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"Asymmetric" scale equations of state are obtained for carbon dioxide and
argon in the critical region, on the basis of which thermodynamic properties
are calculated. Comparison of calculated and experimental data shows that
the error in thermodynamic property description lies within the limits of
experimental uncertainty.

1. Modern methods of describing the thermodynamic properties of fluids in the critical
region are based on the fluctuation theory of phase transitions and critical phenomena [1,
2].

The theoretically based scale equations of state found in the literature [3-6] describe
the unique features of the thermodynamic surface in the asymptotic vicinity of the critical
point. They differ in methods used to introduce nonasymptotic terms, and in their consid-
eration of the asymmetry of the real liquid. These features of the equations are not sig-
nificant from a theoretical viewpoint and essentially reflect the width of the region over
which experimental data can be approximated.

For the equations of [3-6] this range varies from $\Delta\rho = \left|\dfrac{\rho - \rho_c}{\rho_c}\right| \leqslant 0.35$ and $\tau = \dfrac{T - T_c}{T_c} <$

0.04 to $|\Delta\rho| \leq 0.5$ and $\tau \leq 0.2$, but within the range of their own working regions the equa-
tions permit calculating thermodynamic properties in the critical region with an uncertainty
close to that of experiment.

The present study will use the "asymmetric" scale equation of state of [5, 6] to calcu-
late the thermodynamic properties of carbon dioxide and argon. By approximating a limited
quantity of experimental data nonuniversal constants of the equations were determined for
these two substances whereupon calculated and experimental data were compared for a number
of thermodynamic properties.

2. The theoretically based "asymmetric" equation of state of [5] has the following
form:

$$\Delta\mu(r, \theta) = ar^{2-\alpha}\theta(1 - \theta^2) + cr^{2-\alpha+\Delta} +$$

$$+ r^{2\gamma+2\beta-1}[d(1 + e_1 b^4\theta^4) + fb^2\theta^2(1 + e_2 b^2\theta^2)], \tag{1}$$

$$\tau = r(1 - b^2\theta^2), \tag{2}$$

$$\Delta\rho = kr^\beta\theta - B_3\tau = \Delta\eta - B_3\tau. \tag{3}$$

Here $\Delta\mu = [\mu(\rho, T) - M_c(T)]\rho_c/P_c$ is the dimensionless chemical potential; $\tau = (T - T_c)/T_c$
is the dimensionless difference in temperature for the critical T_c; $\Delta\rho = (\rho - \rho_c)/\rho_c$ is the
dimensionless difference of density from the critical ρ_c; r, θ are parametric variables; $\Delta\eta$
is the order parameter.

This equation contains parameters which are universal, critical indices α, β, γ, Δ (in-
dices of isochoric specific heat, the phase equilibrium curve, isothermal compressibility,
and index of the nonasymptotic term, respectively) as well as parameters related to the in-

dividual properties of the material — critical amplitudes, which are defined by processing the experimental data a, c, d, f (coefficients of the asymptotic, nonasymptotic, and asymmetric terms).

The parameters e, e_1, e_2, and b^2 can be defined in terms of universal critical indices with the following expressions:

$$e = 2\gamma + 3\beta - 1, \quad e_1 = \frac{(5 - 2e)(e - \beta)(3 - 2e)}{3(5\beta - e)},$$

$$e_2 = \frac{(5 - 2e)(e - 3\beta)}{3(5\beta - e)}, \quad b^2 = (\gamma - 2\beta)/(1 - 2\beta)\gamma.$$

The coefficient k is related to the critical amplitude of the asymptotic term of the scale equation of state for the phase equilibrium term

$$\Delta\rho_{\text{H}} = \pm B_0(-\tau)^\beta \pm B_1(-\tau)^{\beta+\Delta} + B_2(-\tau)^{1-\alpha} - B_3\tau \tag{4}$$

such that

$$k = (b^2 - 1)/|z_0|^\beta, \tag{5}$$

where $|z_0| = B_0^{-1/\beta}$.

We can easily transform from Eq. (1) to an expression for the free energy:

$$\rho F = P_c[\Psi(r, \theta) + (1 + \Delta\rho)M_0(\tau) + \Phi_0(\tau)], \tag{6}$$

where $\Psi(r, \theta) = \int \Delta\mu d\Delta\eta$ is the singular portion of the free energy, and the regular portions of the chemical potential $M_0(\tau)$ and the free energy $\Phi_0(\tau)$ are represented by polynomials:

$$M_0 = m_0 + \sum_{i=1}^{4} m_i\tau^i, \tag{7}$$

$$\Phi_0 = -1 + \sum_{j=1}^{4} f_j\tau^j. \tag{8}$$

The adjustment parameters dependent on the individual properties of the material are found by approximation of the experimental data on P–ρ–T properties and isochoric specific heat (or the speed of sound) in the range of state parameters $0.65 \leq \rho/\rho_c \leq 1.4$ and $T_S \leq T \leq 1.2\,T_c$, which is the working range of the "asymmetric" scale equation of state, Eqs. (1)-(8) (T_S being the temperature on the saturation line).

In the present study the thermal constants of the state equations k, a, c, d, f, f_i were determined by processing P–ρ–T data by the method of least squares. The values of the coefficients B_i appearing in Eq. (4) were found by preliminary processing of the density on the phase equilibrium curve in the interval $|\Delta\rho| \leq 0.5$. The value of the parameter k was determined in accordance with Eq. (5). The value of the parameter B_3 [see Eq. (3)] was refined by the selection method with the condition of best description of P–ρ–T properties. The caloric coefficients m_i (i = 2-4) appearing in the expansion of the regular portion of the chemical potential in temperature, Eq. (7), were determined by processing the experimental data on specific heat C_V. In the calculations experimental points lying within the region $|\tau| < 10^{-3.5}$ were excluded, because in the usual thermographic method data obtained closer than this to the critical point prove to be distorted because of the hydrostatic effect.

As for the coefficients m_0 and m_1, they are related to the enthalpy and entropy at the critical point:

$$H_c = (P_c/\rho_c)[-f_1 + m_0 - m_1], \tag{9}$$

$$S_c = (P_c/\rho_c T_c)[-f_1 - m_1]. \tag{10}$$

For carbon dioxide these were defined by approximation of tabular values on enthalpy and entropy [7]. This was not done for argon.

TABLE 1. Values of CO_2 and Ar Critical Parameters

Parameter	CO_2 value	95% confidence level	Ar value	95% confidence level
T_c, K	304,126 [19]	— (fixed)	150,66 [16]	—(fixed)
ρ_c, kg/m^3	466,5 [19]	— (fixed)	535,1 [16]	— (fixed)
P_c, MPa	7,375	$\pm 0,005$	4,85	$\pm 0,01$

TABLE 2. Parameters of Scale Equation of State, Eqs. (1)-
(3) for CO_2 and Ar

Parameter	Mean CO_2 value	95% confidence interval	Mean Ar value	95% confidence interval
z_0	0,206	— (fixed)	0,335	— (fixed)
B_3	—0,65	— (fixed)	0,0	— (fixed)
a	21,28	$\pm 0,05$	17,97	$\pm 0,02$
c	—4,95	$\pm 0,10$	—9,7	$\pm 0,4$
d	14,80	$\pm 0,21$	0,16	$\pm 0,62$
f	—21,27	$\pm 0,38$	0,47	$\pm 0,84$
f_1	—6,993	$\pm 0,013$	—5,912	$\pm 0,015$
f_2	23,37	$\pm 0,45$	15,2	$\pm 1,1$
f_3	0,9	$\pm 3,5$	—18,60	$\pm 0,74$
f_4	8,8	$\pm 8,5$	42,8	$\pm 2,6$
m_0	—28,920	$\pm 0,012$	—	
m_1	—62,0920	$\pm 0,057$	—	
m_2	—15,70	$\pm 0,02$	—6,2640	$\pm 0,0092$
m_3	6,74	$\pm 0,11$	17,26	$\pm 0,66$
m_4	—10,40	$\pm 0,22$	—37,2	$\pm 2,3$

The values of the universal critical indices were fixed at their theoretical values: $\alpha = 0.11$, $\beta = 0.325$, $\Delta = 0.5$. The value of the critical index γ was calculated from the universal expression:

$$\gamma = 2(1-\beta)-\alpha.$$

Values of the critical temperature and density were taken from experiment (see Table 1), while the critical pressure value was found by approximation of P–ρ–T data.

3. Before evaluating the results of the approximation, we will characterize the experimental data employed.

To obtain the non-universal parameters of the "asymmetric" CO_2 and Ar equations of state experimental values were used from coexistence curves [8-10], pressure curves [10-14], the isochoric specific heat curves [8, 15-19] in the ranges $0.65 \leq \rho/\rho_c \leq 1.4$ in density and from the saturation line to 1.15 T_c in temperature. The temperature interval was narrowed to 1.15 T_c because of a lack of sufficient experimental material to determine the selection constants at temperatures $T > 1.15$ T_c for isochoric specific heat of CO_2 and argon P–ρ–T properties.

Because of the difference in critical parameters, the experimental data on the coexistence curve [8, 9] as well as the P–ρ–T properties of Ar [11-13] were dedimensionalized using their "own" critical values before processing.

To quantitatively verify the reliability and accuracy of the equations obtained a comparison was made of calculated and experimental values for the speed of sound W [20-22], isobaric specific heat [23], and the derivative $(\partial P/\partial T)_\rho$ [24], none of which were used in choosing the selection constants in the equation of state.

It should be noted that for the P–ρ–T properties and speed of sound the experimental temperature values were first corrected in accordance with the MPTSh-68 temperature scale: for Ar [11-13, 20, 21] the values were increased by 0.077 K in accordance with the suggestions of [25], while for CO_2 [10, 14], following [26], they were reduced by 0.035 K. Moreover, the experimental data on the speed of sound [20, 21] and isobaric specific heat [23], presented in P, T-coordinates were recalculated to ρ–T-coordinates, in which Eqs. (1)-(3) are formulated.
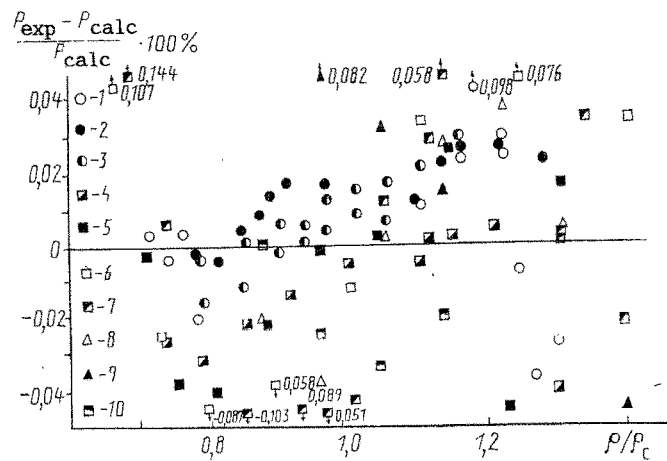
Fig. 1. Deviation of experimental values of CO_2 pressure [10, 12] from calculations on isotherms: 1) $T/T_c = 0.998$; 2) 1.000; 3) 1.001; 4) 1.002; 5) 1.003; 6) 1.012; 7) 1.030; 8) 1.061; 9) 1.145; 10) 1.226.
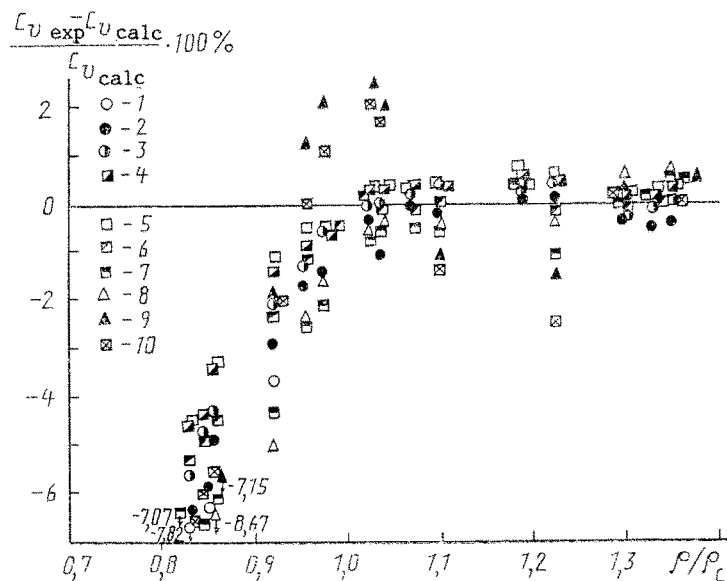

Fig. 2. Deviation of experimental values of CO_2 isochoric specific heat [27, 28] from calculations on isotherms: 1) $T/T_c = 1.227$; 2) 1.211; 3) 1.194; 4) 1.178; 5) 1.161; 6) 1.079; 7) 1.0146; 8) 1.026; 9) 1.006; 10) 1.003.

4. The coefficients of the "asymmetric" scale equations of state for CO_2 and Ar obtained by the approximation are given in Table 2, while comparisons of values calculated on their basis with experiment are shown in Figs. 1-5.

In approximating the data on isochoric specific heat C_V for Ar a parameter value $a = 17.64 \pm 0.06$ was obtained, close to the value obtained by processing of P-ρ-T properties: $a = 17.97 \pm 0.02$. This fact indicates agreement of the data of [11-13] and [8, 15-18] in the asymptotic vicinity of the critical point. The thermal parameters a, c, d, f, $f_{1.2}$ of the Ar "asymmetric" equation of state were fixed at values found from processing of P-ρ-T properties [11-13]. As for the coefficients of the expansion of the regular portion of the free energy in temperature f_3 and f_4, because of a lack of experimental points over pressure for Ar and on the boundary of the working region of the equation of state over temperature their values were refined by repeated minimization over the available experimental isochoric specific heat values. This permitted an improvement in description of the P-ρ-T properties.
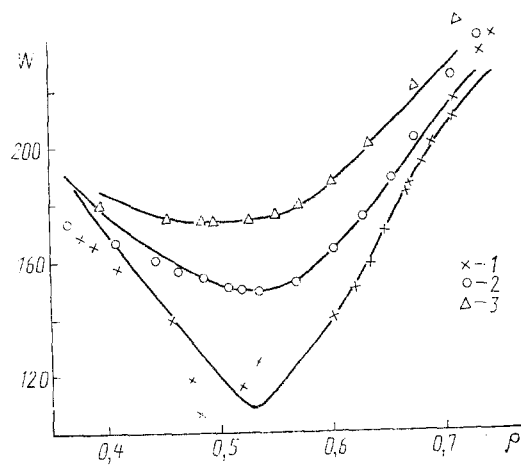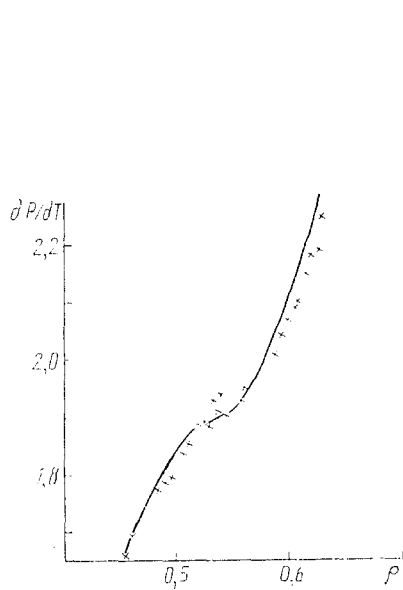
Fig. 3

Fig. 4

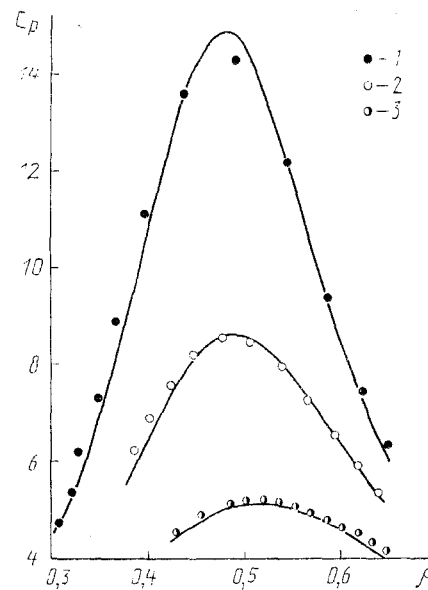Fig. 5

Fig. 3. Speed of sound in argon [20, 21] vs density on isotherms: 1) T/T_c = 1.000; 2) 1.008; 3) 1.019. W/m/sec; ρ, g/cm^3.

Fig. 4. Experimental data on derivative $(\partial P/\partial T)_\rho$ in Ar [24] compared to calculated data (solid line) on critical isotherm. $\partial P/\partial T$, bar/K.

Fig. 5. Experimental data on isobaric specific heat of CO_2 [23] compared to calculated data (solid line): 1) P = 8.826 MPa; 2) 9.856; 3) 11.768. C_p, kJ/(kg·K).

The mean deviation of the experimental pressure values from calculation comprised 0.02-0.03% for CO_2, excluding the isotherm T/T_c = 1.03 (Fig. 1), and 0.05-0.01% for Ar, excluding 10 points on the limiting isotherms of 1.148 T_c and 1.082 T_c, for which the deviation reaches 0.5-1.0% due to insufficiency of the experimental data in the range T > 1.05 T_c as compared to the entire data mass.

Moreover, for CO_2 a variant was calculated with renormalized temperature $\tau^* = \tau(T_c/T) = 1 - T_c/T$ [with free energy also renormalized, $\rho F^* = \rho F \cdot (T/T_c)$]. Calculation showed that renormalization permits expansion of the range of description of experimental P—ρ—T data to 1.3 T_c in temperature.

The mean deviation of the experimental values of specific heat C_V from calculation for Ar comprises 1-1.5% and reaches 3-5% at the boundary of the working region of the equation of state on the low density side.

The error in describing isochoric specific heat of CO_2 was equal to the experimental uncertainty, comprising 2% for $\tau \le 10^{-3}$ and less than 0.5% in the range $\tau \le 0.15$. To determine the caloric constants of the equation data on isochoric specific heat on the critical isochor we used [19].

Processing of experimental C_V data [27, 28] revealed systematic deviations of the experimental values from computation on the precritical isochors which reached 10% (Fig. 2). This fact agrees with the results of Altunin's analysis [29] and confirms the conclusion of the methodical unreliability of the experiments of [27, 28] in this region.

Figures 3-5 show deviations of experimental values from calculation for the speed of sound and the derivative $(\partial P/\partial T)_\rho$ in argon, as well as the isobaric specific heat C_p of carbon dioxide.

Processing of experimental data on the speed of sound in Ar was carried out on 12 isotherms. The mean deviation of experimental values from calculation comprised 2%, reaching 5-7% on the edges of the approximation region with regard to density, especially in the direction of the gas, on the critical and close-lying isotherms. As is evident from Fig. 3, the calculated values of the positions of the minima for isotherms closest to the critical are shifted in the direction of higher densities as compared to experiment, which naturally leads to increase in the error of the description. It could be proposed that displacement of the minima on the isotherms close to critical for Ar is related to a difference between the critical parameters presented in [16] (see also Table 1) and in [20, 21]. Moreover, it should be kept in mind that at $|\tau| < 10^{-3}$, according to [20, 21] the experimental uncertainty rises abruptly from 0.5 to 5%.

Experimental data on the derivative $(\partial P/\partial T)_\rho$ for Ar [24] are described within 2%, which corresponds to the experimental accuracy (Fig. 4).

For CO_2 the mean deviation of experimental values of isochoric specific heat [23] from calculation comprises 0.5-1% (Fig. 5) while the corresponding figure for speed of sound [22] is 2%, which lies within the limits of experimental uncertainty.

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A TRANSVERSELY BLOWN ARC DISCHARGE IN A PLASMATRON

WITH COAXIAL ELECTRODES

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A discharge is investigated of an alternating current in a plasmatron with "hot" coal graphite electrodes, the faces of which are located in one plane. Experiments are described with a segmented external electrode. On the basis of an analysis of the oscillograms of current in the electrode segments and of photographs of the front part of the plasma tip it is concluded that the burning of the discharge cannot be in the form of a solitary arc and that the discharge is comprised of a system of arcs. Calculation of the volt—ampere characteristics of the transversely blown off diffuse discharge showed the impossibility of its burning in the conditions under consideration.

In a series of industrial electric arc devices, the discharge takes the form of a system of parallel arcs operating from one voltage source [1-3]. In [4] the questions of the analysis, modeling, and synthesis of multi-arc systems are examined for the first time. It is observed that on a smooth cylindrical electrode a stationary division of the arc was not achieved experimentally. Segmentation of the discharge in [4] is achieved by embedding thermo-emissive inserts into the body of the electrode. It is shown that stable burning of the radial elements of the segmented discharge is guaranteed by their rising volt—ampere characteristics, but the cause of the division of the discharge is the radial flux of the gas jet toward the walls of the electrode.

In the present work a discharge in a plasmatron with "hot" electrodes [5] is investigated. Experimental observation of the operation of the device allows one to propose that in