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MODIFIED LEUNG–GRIFFITHS EQUATION FOR DESCRIBING THE THERMODYNAMIC PROPERTIES OF A CO_2–Ne SOLUTION NEAR THE CRITICAL POINT OF CO_2 VAPORIZATION

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A scaling equation of state is proposed, allowing for the asymmetry of the actual liquids and their nonasymptotic behavior with greater distance from the critical point. Experimental data for CO_2–Ne solutions near the critical point of CO_2 vaporization are approximated with this equation.

Binary solutions near the critical points of vaporization of the pure solvent have a number of characteristic properties. Even at very low concentrations there is a region of temperatures and pressures at which molecules of the dissolved substance interact with each other so strongly that the solution becomes essentially nonideal. The compressibility of the system and the derivative of the concentration of the component with respect to its chemical potential increase strongly in the critical region, which leads to peculiarities of the kinetic properties such as diffusion and thermal conductivity (thermal diffusivity) and to an increase in fluctuations of concentration and density, while the partial molar volume of the solvent can even assume negative values [1]. The complexity of the description of critical phenomena in such solutions is due primarily to the existence of two strongly fluctuating order parameters, connected with the density and concentration. At the same time, the situation is simplified to a certain extent by the presence in this region of an additional small parameter — the concentration of the dissolved substance. The latter made it possible in [2, 3] to propose equations of state of the type of a Landau expansion in powers of the concentration and the departures of the temperature and density from the critical values for a pure solvent, as well as an equation of state based on the fluctuation theory of phase transitions of the second kind, from which the renormalization of the critical indices follows [4].

Several equations of state for the description of the thermodynamic properties of a binary solution in the region near the entire critical line of vaporization have also been proposed up to now. These are, primarily, the van der Waals equation of state [5] and the Leung–Griffiths [6] and Kiselev [7] equations.

The CO_2–Ne solution near the critical point of CO_2 was investigated for the further

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TABLE 1. Coefficients of the Equation of State (1) for CO_2—Ne Solutions

P_c, MPa	7,38609±0,00333	$A_{T^2}\cdot 10^3$, MPa/°K^2	1,628±0,719
A_T, MPa/°K	0,16228±0,00341	$A_{T\rho^2}\cdot 10^7$, MPa·m^6/°K·kg^2	8,74±5,76
A_N, MPa	43,361±0,214	A_{NT}, MPa/°K	0
$A_{T\rho}\cdot 10^4$, MPa·m^3/K·kg	3,530±0,285	$A_{N\rho^2}\cdot 10^4$, MPa·m^6/kg^2	2,351±0,628
$A_{N\rho}$, MPa·m^3/kg	0,1557±0,0034	σ, MPa	0,010898
$A_{\rho^3}\cdot 10^8$, MPa·m^9/kg^3	0,76±1,14		

development of the problem of an adequate description of the thermodynamic properties of binary solutions near the critical point of vaporization of the solvent. Experimental P—ρ—T—N data for this solution were obtained by the procedure described earlier [8]. We only explain that the measurements were made in a variable-volume piezometer with windows for observation of the phase separation. To eliminate the gravitational effect and rapidly bring the investigated solution to thermodynamic equilibrium, the piezometer was equipped with a magnetic stirrer. The pressure was measured with a piston-load manometer with an error of 0.01 MPa, while its variation relative to the critical value was measured with a far higher accuracy, 0.00025 MPa. The temperature was measured with a platinum resistance thermometer with an error of 0.01°K, while its variation relative to the critical temperature was measured to within 0.0005°K. The error in determining the density of the solution was 1 kg/m^3, while the error in determining the concentration was from 0.008 to 0.02 mole % Ne. We investigated 19 solutions with different concentrations and obtained 462 points in P—ρ—T—N space in the ranges of temperatures of 302-309.5°K, of densities of 392-568 kg/m^3, of concentrations of 0-5.076 mole % Ne, and of pressures of 7.2-9.7 MPa. The experimental data obtained are presented in [9] in the form of tables.

For the preliminary treatment of the experimental data, we used an equation of state based on the assumption that the thermodynamic potential is analytic [10]:

$$P = P_c + A_T\Delta T + A_N N + A_{T\rho}\Delta T\Delta\rho + A_{N\rho}N\Delta\rho + A_{\rho^3}\Delta\rho^3 + \\ + A_{T^2}\Delta T^2 + A_{T\rho^2}\Delta T\Delta\rho^2 + A_{NT}N\Delta T + A_{N\rho^2}N\Delta\rho^2. \quad (1)$$

To describe the asymmetry of an actual solution, Eq. (1) contains additional terms in comparison with the equations of state proposed earlier [2]. A detailed investigation of the significance of the different terms in Eq. (1) was made in [9]. The best approximation of the experimental data corresponds to the values of the coefficients presented in Table 1. The confidence intervals are determined by the combined confidence region of variation of the parameters for the 0.68 confidence level (confidence probability). For the independent determination of the confidence intervals of each parameter separately, their values approximately correspond to 0.99 confidence [11]. The addition of asymmetric terms to the equations of state proposed earlier [2] leads to a pronounced decrease in the departures of the experimental points from the calculated values. Nevertheless, an analysis of these departures shows that they continue to have a systematic character, and consequently, despite the relatively small error of approximation (∿0.1%), Eq. (1) cannot be considered adequate to the experimental data. The inadequacy evidently is a consequence of the fact that this equation is based on the assumption of the absence of peculiarities in the behavior of the thermodynamic quantities near the critical point, whereas numerous experiments confirm the existence of singularities due to anomalous fluctuations in concentration and density [12]. Equation (1), obtained within the framework of self-consistent field theory, is still distinguished by comparative simplicity and has a relatively small approximation error (∿0.1%), which permits its use as an interpolation equation for the calculation of certain thermodynamic properties of the CO_2—Ne binary solution in the above-indicated region of variation of the parameters of state.

To obtain an adequate description of the properties of binary solutions in the investigated region of state we used the hypothesis of isomorphism of the fluctuation theory of phase transitions [4], the essence of which, as is well known, consists in the assumption that the peculiarities of the behavior of the thermodynamic potential of a system are retained upon the introduction of additional degrees of freedom (the concentration in our case) if the fields associated with these variables (the chemical potential) are fixed. The above-mentioned equations of state of [6] and [7] were proposed on the basis of this hypothesis. However, the equation of [6], satisfactorily describing the ^3He—^4He solution near the critical line of vaporization, and the equation of [7] yield a low accuracy of approximation in the case of solutions of the CO_2—inert-gas type if one does not introduce a comparatively large number of parameters (fitting terms) into the regular parts of the equation of state. Concerning the equation of state from [7], it should be mentioned that it practically consists of a series of separate equations, each of which describes the P—ρ—T dependence of a solution with a given concentration, and therefore it is ill suited for determining such dependences for solutions with arbitrary concentrations.

The assumption was made that the necessity of introducing a large number of fitting parameters is a reflection more of the nonasymptotic behavior of the singular parts than of the regular ones, and of the asymmetry, inherent to the solvent, with respect to the behavior of the thermodynamic functions of the Ising model (of a magnetic substance). Thus, for an adequate approximation one must allow for the nonasymptotic behavior and (correctly) the asymmetry. For the solution of this problem, terms were added to the equation of state by a method similar to that used earlier to refine the equation of state of a pure liquid [13]. As the start we used the Leung—Griffiths equation under the assumption that its singular part, with the addition of nonasymptotic terms, can be written in parametric form in the isomorphic variables h_1, h_2, A_1, and A_2,

$$h_1 = Ar^{\gamma+\beta}\theta(1-\theta^2), \tag{2}$$

$$h_2 = r(1-B^2\theta^2), \tag{3}$$

$$A_1 = gr^{\beta}\theta - \frac{Eg}{A}r^{\beta+\Delta}\varphi(\theta), \tag{4}$$

$$A_2 = Agr^{1-\alpha}(s_0+s_2\theta^2) + Egr^{1-\alpha+\Delta}Q_0, \tag{5}$$

where $B^2 = (\gamma-2\beta)/\gamma(1-2\beta)$; $s_0 = \gamma(\gamma-1)/2B^2\alpha(1-\alpha)$; $s_2 = -\gamma(1-2\beta)/2\alpha$; $Q_0 = -\gamma(\gamma+\Delta)/2B^2(1-\alpha+\Delta)$;

$$\varphi(\theta) = \frac{\theta[1-B^2\theta^2(1-2\beta)]}{1+\theta^2[B^2(2\gamma+2\beta-1)-3]+\theta^4B^2(3-2\gamma-2\beta)}.$$

Using Eqs. (2)-(5), one can find an expression for the thermodynamic potential π, which is defined by the equation

$$d\pi = A_1dh_1 + A_2dh_2,\ \pi = Agr^{2-\alpha}(z_0+z_2\theta^2+z_4\theta^4) + Egr^{2-\alpha+\Delta}(p_0+p_2\theta^2). \tag{6}$$

Here $z_0 = (\gamma-2\beta-\gamma\alpha B^2)/2B^4\alpha(1-\alpha)(2-\alpha)$, $z_4 = (\gamma+\beta-3/2)/\alpha$, $z_2 = [\alpha B^2(2\gamma+2\beta-1)-\gamma+2\beta]/2B^2\alpha(1-\alpha)$, $p_0 = -(\gamma+\beta)/2B^2(2-\alpha+\Delta)\times(1-\alpha+\Delta)$, and $p_2 = (1-2\beta)/2(1-\alpha+\Delta)$. The following new variables were introduced in [6] to describe a two-component system: $\tau = 1/RT_c - 1/RT$, $\zeta = C_1\exp(\mu_1/RT)/[C_1\exp(\mu_1/RT) + C_2\exp(\mu_2/RT)]$, $h = \ln[C_1\exp(\mu_1/RT) + C_2\exp(\mu_2/RT)] - H(\zeta,\tau)$.. The function H(ξ, τ) is chosen in the form of a polynomial of ξ and τ in such a way that the field h equals zero over the entire two-phase equilibrium surface and on the critical isochors in the one-phase region:

$$H(\zeta,\tau) = b_0 + b_1\zeta + b_2\zeta(1-\zeta) + (g_0+g_1\zeta)\tau. \tag{7}$$

For the conversion from the isomorphic variables τ, h, and ξ we used the relations [12] $\tau = a_0(h_2 - bh_1)$ and h = h_1. The expression for H(ξ, τ) was simplified somewhat: $H(\zeta,\tau) = b_0 + b_1\zeta + b_2\zeta(1-\zeta) + g_0\tau$. The variable ζ remained unchanged. The use of such transformations enabled us to write the equation of state in the form

$$P = \omega(\zeta, h, \tau)RT, \tag{8}$$

$$\rho = \omega_h^{\mathrm{reg}} + \Delta\rho, \tag{9}$$

$$T = [R(a_0 + a_1\zeta - a_0\tau)]^{-1}, \tag{10}$$

$$N = \zeta + \zeta(1-\zeta)[(\omega_\zeta + a_1\omega_\tau)/\rho - v_1]. \tag{11}$$

Here the subscript denotes differentiation of these quantities with respect to the corresponding variable, $\omega = \omega^{\mathrm{reg}} + \omega^{\mathrm{sing}}$, $\omega^{\mathrm{reg}} = c(\zeta) + d_0\tau + l_0\tau^2 + f(\zeta)h$, $\omega^{\mathrm{sing}} = f(\zeta)\pi$, $c(\zeta) = c_0 + c_1\zeta$, $f(\zeta) = f_0 + f_1\zeta$, and $\Delta\rho$ is defined, in accordance with [12], by the expression $\Delta\rho = f(\zeta)(A_1 + bA_2)$, i.e.,

$$\rho = (f_0 + f_1\zeta)\left[1 + gr^{\beta}\theta - \frac{Eg}{A} r^{\beta+\Delta}\varphi(\theta) + bAgr^{1-\alpha}(s_0 + s_2\theta^2)\right]. \tag{12}$$

Thus, the pressure, density, temperature, and concentration of the system are determined by the three parameters r, θ, and ξ, varied in the intervals of $0 \leqslant r \leqslant \infty$, $-1 \leqslant \theta \leqslant +1$, and $0 \leqslant \xi \leqslant 1$.

As we see, Eqs. (8)-(11) are a modification of the Leung–Griffiths equations [6]. By contrast with the latter, in them asymmetry is taken into account by the method proposed in [12], and nonasymptotic terms are added. The regular parts of the equations of [6] were also subjected to certain unessential changes. In particular, since the data approximated by this equation were obtained near the critical point of the pure solvent, the regular part of the potential ω was chosen in the form of the simplest polynomials of ζ, permitting a decrease in the number of fitting parameters.

The equation of state (8)-(11) was used to approximate experimental P–ρ–T–N data for a CO_2–Ne binary gas solution [9, 17]. Some of the coefficients of the equation were determined directly from the experimentally obtained critical values of the pressure, temperature, and density of pure CO_2: $a_0 = 3.95445 \cdot 10^{-4}$ kmole/kJ, $c_0 = 2.92030$ kmole/m^3, $f_0 = 10.6346$ kmole/m^3.

At present it is assumed that the critical indices of classical liquids coincide with the indices of the Ising three-dimensional, one-component model [14, 15], and therefore in approximating the experimental data by the equation of state (8)-(11) obtained, we fixed the theoretical values of the critical indices $\beta = 0.325$, $\gamma = 1.24$ [12], and $\Delta = 0.45$ [16]. Moreover, varying the indices β, γ, and Δ within fairly wide limits showed that this does not result in a significant improvement in the description of the experimental data. And since parameters β, γ, and Δ appearing nonlinearly in the equation considerably increase the calculation time, fixing them seemed fully justified. The remaining coefficients of the equation of state (8)-(11) were determined by the method of minimizing the sum of the squares of the departures of the pressure, density, temperature and concentration from their experimental values:

$$\Phi = \sum_{i=1}^{M} [\Phi_i + W_N^*(N_i^{\mathrm{e}} - N_i^a)^2], \tag{13}$$

where $\Phi_i(\zeta_i, r_i, {}^{\mathrm{e}}\theta_i) = W_P[P_i^{\mathrm{e}} - P(\zeta_i, r_i, \theta_i)]^2 + W_\rho[\rho_i^{\mathrm{e}} - \rho(\zeta_i, r_i, \theta_i)]^2 + W_T[T_i^{\mathrm{e}} - T(\zeta_i, r_i, \theta_i)]^2 + W_N [N_i^a - N(\zeta_i, r_i, \theta_i)]^2$. The values of the parameters ξ_i, r_i, and θ_i for the i-th point were determined by minimizing $\Phi_i(\zeta_i, r_i, \theta_i)$ with respect to these parameters. The values of the weights W_P, W_ρ, W_T, W_N, and W_N^* were chosen in such a way that the contributions of the respective terms to the sum of the squares of the deviations were of the same order. The fitting values N_i^a were taken as constants for each concentration separately. Points from the one-phase region and points lying on the boundary curve and in the two-phase region took part in the treatment.

The coefficients found by the method of least squares and their combined confidence intervals have the following values: $g = 1.193 \pm 0.04$; $A = 6.26 \pm 0.6$; $E = -2.1 \pm 4.6$; $b = -0.050 \pm 0.076$; $\nu_1 = 2.29 \pm 0.90$; $a_1 = (6.82 \pm 4.6) \cdot 10^{-5}$ kmole/kJ; $c_1 = 34.7 \pm 24$ kmole/m^3; $d_0 = (44.24 \pm 0.3) \cdot 10^3$ kPa; $l_0 = (-4.9 \pm 1.0) \cdot 10^8$ kJ^2/kmole·m^3; $f_1 = 23.7 \pm 16$ kmole/m^3. The rms errors in approximating the pressure, density, temperature, and concentration by Eq. (8)-(11) are $\sigma_P = 0.0015$ MPa, $\sigma_\rho = 0.005$ kmole/m^3, $\sigma_T = 0.0031$°K, and $\sigma_N = 0.02$ mole % Ne. The combined confidence intervals were determined under the assumption of a parabolic dependence of the error functional (13) on the parameters being fitted, since there is considerable difficulty in finding the true dependence for a system of nonlinear equations with a large number of parameters. As a result, the confidence intervals evidently proved to be overstated. This is indicated by the fact that an attempt to approximate the experimental data by Eq. (8)-(11) without the terms containing, e.g., the parameters b and E led to a pronounced increase in the rms approximation errors, although the confidence intervals for some of these parameters proved to be larger than the very values of the parameters.

It must be noted that the accuracy of approximation of the experimental data by the equation of state proposed in this paper is higher than that by an equation of state of the Leontovich–Rozen type, and it approaches the accuracy in obtaining the experimental data with a relatively small number of varied parameters. In this respect the equation of state (8)-(11) also differs advantageously from the equation proposed in [7], which is unsuited for finding the dependence of the thermodynamic quantities on the concentration and has an approximation error comparable with the error of an equation of state of the Leontovich–Rozen type.

NOTATION

P, pressure, MPa; ρ, density, kg/m^3; T, temperature, °K; N, concentration, molar fractions; σ, rms error of approximation; ΔT, $\Delta\rho$, deviations of the temperature and density from the critical values for pure CO_2; r and θ, Scofield "radial" and "angular" variables; g and A, constants of the Scofield equation; E, constant to the nonasymptotic term; a_o and b, constants of the connections between the isomorphic variables h_1 and h_2 and the variables h and τ; R, gas constant; π, thermodynamic potential; τ, h, ξ, variables of the parametric equation of state; μ_1 and μ_2, chemical potentials of the first and second components: C_1 and C_2 constants of the connections between ξ and μ_1 and μ_2. Critical indices: α, heat capacity; γ, compressibility; β, boundary curve; Δ, nonasymptotic part.

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