Phenomenological Method for Construction of the Liquid and Gas Equation of State[†]

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The semiempirical method was suggested for construction of a simple equation of state for liquid and gas. With this purpose, some new conditions and restrictions, which should be satisfied by the “right” equation of state, were formulated. In particular, the preferable structure of the equation of state was determined. The equations for description of thermodynamic properties of real gases and liquid phase were derived with involvement of additional restrictions. The second virial coefficient calculated on the basis of the modified step potential of intermolecular interactions was used as the temperature functions in the derived equations, and the density functions were determined from analysis of experimental data. A new equation of state for liquid and gas with six individual adjustable parameters was suggested. This new equation describes the thermodynamic properties of substances much better than the known Benedict−Webb−Rubin equation of state. Some caloric properties of substances were calculated.

Introduction

Among the majority (more than 200) of available equations of state, only a few can be considered as the equations of state suitable for the description of thermodynamic properties of liquid, gas, and fluid. Most of these equations do not allow calculation of caloric and thermal properties of substances in a wide range of state parameters with the acceptable accuracy (except equations of state with tens and hundreds of adjustable coefficients). The most famous among simple equations of state are the van der Waals and Benedict−Webb−Rubin equations; the former is known as the most physically grounded, and the latter is known as the most accurate of the low-parametrical equations of state.

It is known that both theoretical and empirical methods of equation of state derivation do not give satisfactory results.[1] We guess that the most preferable is the approach where the functional form and structure of equations can be achieved via theoretical and physical considerations. The specific form of analytical expressions and numerical values of included parameters can be determined with the help of experimental data.

At this, we proceed from a fundamental understanding of the fact that there are no principle differences in the characters of heat motion in liquid and gas. There are several factors which allow the assumption that the mechanisms of heat motion in liquids and gases differ insignificantly, and in the first approximation, they can be considered similar. In this case, the search for the simple equations of the liquid and gas state becomes not only possible but also physically grounded.

It is known that the “right” equation of state should meet some physical and mathematical conditions and restrictions. The more such restrictions and conditions are imposed on the sought equation of state and the stricter these conditions are, the simpler the purposeful semiempirical search for the equation of state of liquid and gas for a single-component substance is. Most of these conditions are common and follow from the differential equations of equilibrium thermodynamics. However, in the literature, such a principle question as the structure (form) of the state equation has not been solved yet.

In previous papers, the authors have formulated some conditions and restrictions, which supplement the existing ones and simplify significantly the search for simple equations of state of liquid and gas for the satisfactory description of thermodynamic properties of a single-component substance. The brief description of our main results is presented below.

Methods for Derivation of Semiempirical Equation of State of Liquid and Gas

1. The preferable structure of the equation of state obligatory for all individual substances is determined.[2] It is shown that the equation for the compressibility factor of a single-component substance should include a summand, which is the function of density only. This conclusion follows from the known energy equation

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \text{ or } \left(\frac{\partial U}{\partial V}\right)_T = \frac{RT^2}{V}\left(\frac{\partial Z}{\partial T}\right)_V \qquad (1)$$

Then it follows that

$$Z = \int \frac{V}{RT^2}\left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}T + \psi(V) = \varphi(T, V) + \psi(V) \qquad (2)$$

Here, T is temperature; $V = 1/\rho$ is specific volume; ρ is density; P is pressure; U is specific internal energy; $Z = (PV)/(RT)$ is the compressibility factor; and $R = (R_0/\mu)$ is the gas constant of the substance.

The most common and physically grounded equation satisfying condition 2 is van der Waals equation of state

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$$Z(T, V) = \frac{V}{V - b} - \frac{a}{VRT} = 1 + \frac{b}{V - b} - \frac{a}{VRT} \tag{3}$$

It follows from eq 3 that function

$$Y = Z + \frac{a}{VRT} = 1 + \frac{b}{V - b} = \psi(V) \tag{4}$$

in the first approximation should be the function of density only, and this is proved by our calculations (Figure 1). However, the coefficient in the numerator of the second summand in eq 4 can hardly be taken equal to b (in the denominator), and at optimal description of the initial data array, it differs from b by a factor of 2−3. The modified van der Waals equation of state can be written as

$$Z = 1 + \frac{c}{V - b} - \frac{a}{VRT} \tag{5}$$

where $c = (2...3)b$.

Equation 5 describes reference (averaged experimental) data 5−10 times more accurate than the initial (eq 3) van der Waals equation of state.[2] According to comparison of eqs 3 and 5, the physical sense of coefficients "a" and "b" in eq 5 stays the same as in the van der Waals equation of state (eq 3). The density function ψ(v) describes the asymptotic behavior of compressibility factor Z at $T \rightarrow \infty$. In the first approximation function, $\psi(V)$ at densities below the critical one can be described by the hard spheres equation of state[1,3] (see Figure 1). However, with expansion of the density range, the description of function $\psi(V)$ by the hard spheres equation becomes inadequate.

For optimal description of experimental data on thermal properties of various substances depending on the range of state parameters and features of the studied substance, we have used different approximations for description of the function $\psi(V)$.

2. The modified step potential of intermolecular interactions is described early.[4,5] This potential is the superposition of hard sphere potential, one or several barriers, potential well, and London potential; the London potential describes interaction between molecules at large distances. By means of this potential, we have derived the equation for the second virial coefficient $B(T)$ of substances with nonpolar molecules.

$$B(T) = -\frac{A}{T} - c_2(e^{-\beta/kT} - 1) - c_1(e^{\varepsilon/kT} - 1) + b \tag{6}$$

Here, k is Boltzmann constant, and A, b, β, ε, b, c_1, and c_2 are individual constants of substances. This equation in a wide range of temperatures describes $B(T)$ of the large scope of substances within experimental data error. Comparison of $B(T)$ for helium calculated by eq 6 with data[6] is shown in Figure 2 as an example; the second virial coefficient of helium was studied in the largest relative temperature range.

To calculate $B(T)$ of substances with polar molecules, the step potential should be supplemented with the Keesom potential.[3] Results of this calculation are shown in ref 5.

3. To achieve the equation of state for real gases, we have used the idea[7] about possible presentation of the compressibility factor in the form of the sum, where each summand is the product of temperature function and density (volume) function (Kazavchinsky equation)

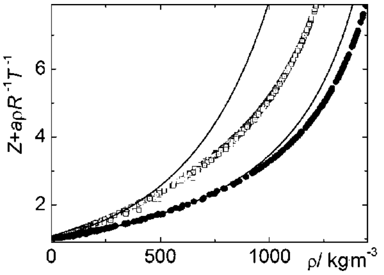

Figure 1. Dependence of function $Y = Z + a/VRT$ on density ρ. • are data for argon, ref 15; □ are data for carbon dioxide, ref 12; lines are calculation by the hard spheres equation of state.

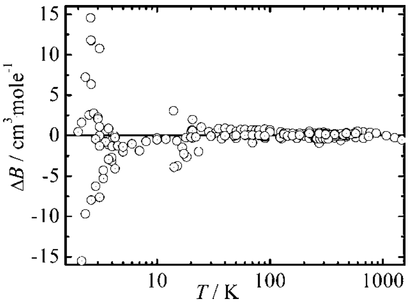

Figure 2. Deviation of the second virial coefficient $B(T)$ calculated for helium from experimental data (ref 6). $\Delta B(T) = B_{\mathrm{exp}} - B_{\mathrm{calc}}$.

$$Z = 1 + F(T)\varphi(\rho) + ... + \psi(\rho) \tag{7}$$

It becomes possible (and sufficient) to use in eq 7 the second virial coefficient, formula 6, as the temperature function. The description close to the optimal one is achieved at $\beta = \varepsilon = T_C/k$. In this case, the equation of state for the real gas of nonpolar substances will take the form

$$Z = 1 - c_1(e^{-\tau} - 1)\omega - c_2(e^{\tau} - 1)\omega\varphi(\omega) - c_3\tau\omega + c_4\tau\omega\varphi(\omega) + c_5\omega e^{c_6\omega} \tag{8}$$

Here, the last summand is one of the possible approximations of function $\Psi(\rho)$ in equations of type 7. According to analysis of experimental data on thermal properties of a wide scope of standard substances, function $\varphi(\omega)$ can be described by the interpolation equation

$$\varphi(\omega) = 1 - 2\omega + 3\left(\frac{1}{2} - Z_c\right)\omega^2 + 4\left(Z_c - \frac{1}{6} - Z_c^2\right)\omega^3 - c_0\omega^5 \tag{9}$$

Here $c_0...c_6$ are adjustable coefficients; $\omega = \rho/\rho_c$ is reduced density; and $\tau = T_c/T$ is reduced reverse temperature.

According to our calculations,[8−11] eq 8 together with 9 describes experimental (reference) data for some substances at temperatures of up to 1000 K, pressures of up to 100 MPa, and densities of up to $1.5\rho_c$ with the error close to the experimental error, excluding the critical area. Comparison of carbon dioxide density calculated by eq 8 with reference data[12] is shown in Figure 3 as the example. This equation allows reliable extrapolation far beyond the limits of the "reference" region, including the area of metastable states.[9,11]

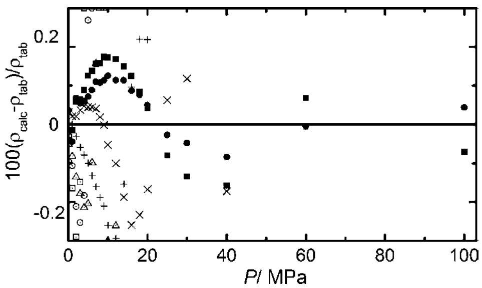

Figure 3. Relative deviations of carbon dioxide densities calculated by eq 8 from data in ref 12: □, $T = 280$ K; ○, $T = 300$ K; Δ, $T = 320$ K; +, $T = 350$ K; ×, $T = 400$ K; ■, $T = 600$ K; ●, $T = 1000$ K.

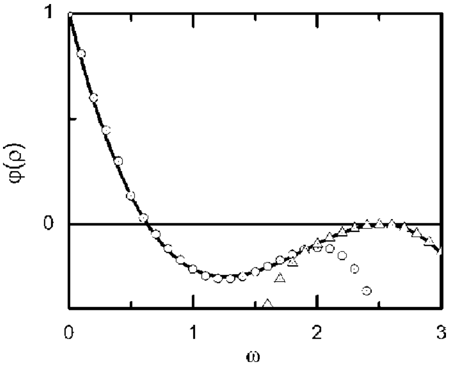

Figure 4. Function $\varphi(\rho)$: line is suggested in the current paper (see eq 11): ○, is used in ref 8; Δ, is used in ref 14.

Equation of State for Liquid and Gas

The above results were used for derivation of simple physically grounded equations of state for liquid and gas.

It is evident that any "right" equation of state at $\rho \rightarrow 0$ should turn into the equation with the second virial coefficient. Thus, in the equation of type 7, temperature functions should be the same, and density functions in eq 7 can differ for gas and liquid and in the fluid equation of state.

If we use the second virial coefficient as the temperature function like in eq 6, the equation of state of gas, liquid, and fluid can be written in general form as

$$Z = 1 - c_1(e^{-\tau} - 1)\rho - c_2(e^{\tau} - 1)\rho\varphi_i(\rho) - c_3\tau\rho + c_4\tau\rho\varphi_i(\rho) + \psi(\rho) \quad (10)$$

Here, $\varphi_i(\rho) = \{\varphi_g(\rho), \varphi_L(\rho), \text{and } \varphi(\rho)\}$ for real gas, liquid, and fluid, respectively.

The density function for the gas phase $\varphi_g(\rho)$ is presented above in eq 9. The density function for the liquid phase $\varphi_L(\rho)$, included in eq 10 in the range of densities above $1.5\rho_c$, is shown as expansion by density degrees in a vicinity of the triple point.[13,14] The liquid phase thermal equation describes thermodynamic properties of some standard substances mainly within the experimental error.

Then, to derive the combined equation of state,[14] density functions $\varphi_L(\rho)$ and $\varphi_g(\rho)$, included in the equations of state for liquid and gas, were joined together. The density functions for the gas and liquid areas are shown graphically in Figure 4. The combined equation describes thermal properties of liquid, gas, and fluid of nonpolar and polar substances within experimental data error, excluding the critical area.

Thus, previous analysis and calculations demonstrated the principle possibility for derivation of the simple equation of state for liquid and gas in the framework of the developed approach. This equation should precisely describe thermodynamic properties of substances in a wide range of densities at moderate pressures and temperatures.

It is obvious that at the search for density functions in the equation of type 10 it is necessary to take into account corresponding physical considerations and restrictions. Besides, it is evident that alternative equations for $\varphi(\rho)$ in eq 10 obtained via approximation of experimental data can differ from each other significantly within the experimental error. One of the possible approximation equations for function $\varphi(\rho)$ in the equation of state of type 10 for liquid, gas, and fluid is written as (see also Figure 4)

$$\varphi(\omega) = -\frac{(\omega_{tr} - \omega)^2(4\omega - \omega_{tr})}{\omega_{tr}^3} \quad (11)$$

Then, the simple equation of state for liquid, gas, and fluid after some changes can be written in reduced variables as

$$Z = 1 + a_1(e^{\tau} - 1 - \tau)(\omega_{tr} - \omega)^2(4\omega - \omega_{tr})\omega - a_2\omega(e^{-\tau} - 1) - a_3\omega\tau + \frac{a_4\omega}{1 - a_5\omega} + \frac{a_6\omega^3}{(1 - a_5\omega)^3} \quad (12)$$

Two last summands in eq 12 are approximations of the density function in the equation of type 2. Equation 12 includes six empirical adjustable parameters and three characteristics of the studied substance: critical temperature T_C and substance density at critical ρ_C and triple ρ_{tr} points. Equation 12 describes qualitatively true the thermodynamic surface and thermal properties of standard substances with the error close to the error of experimental (reference) data (excluding the critical area).

Comparison of Thermal Properties with Experimental and Reference Data

The new equation of state (eq 12) was checked on substances with well coordinated experimental data and standard "fundamental" state equations: argon,[15] nitrogen,[16] and carbon dioxide.[12] The coefficients in eq 12 were determined via minimization of deviations of calculated compressibility factor Z from reference data[12,15,16] by the least-squares method

$$\sigma = \sqrt{\frac{\sum (Z_{tab} - Z_{calc})^2}{N}}$$

Calculated coefficients of eq 12 for some substances are shown in Table 1. Results of a more detailed comparison of calculated thermal characteristics of argon with reference data[15] are shown below.

The absolute average deviation of argon densities calculated by eq 12 with coefficients given in Table 1 from reference data[15] is

$$\text{AAD} = \frac{\sum |\rho_{tab} - \rho_{calc}|}{\rho_{tab}N} \cdot 100\ \% = 0.26\ \%$$

The deviation calculated by the same data array by the known eight-parametrical Benedict−Webb−Rubin equation (BWR) is AAD = 0.52 %. The compressibility factor of argon at the

Table 1. Coefficients of Equation 12 and Parameters in Critical Point (ρ_C, T_C) and $\omega_{tr} = \rho_{tr}/\rho_c$ Reduced Density in Triple Point for Argon, Nitrogen, and Carbon Dioxide

substance	a_1	a_2	a_3	a_4	a_5	a_6:	ω_{tr}	ρ_c $\text{kg}\cdot\text{m}^{-3}$	T_C K
argon[15]	0.019672	0.734282	1.911488	0.512795	0.218464	0.013049	2.645202	535.6	150.687
nitrogen[16]	0.017091	0.901713	2.037046	0.529832	0.222948	0.011132	2.768023	313.3	126.192
carbon dioxide[12]	0.034737	1.913593	2.698302	0.522005	0.169532	0.030696	2.520381	467.6	304.128

critical point is $Z_C = 0.2879$; and this factor calculated by the BWR equation is $Z_C = 0.2208$; and the reference (standard) value[15] is $Z_C = 0.2895$.

According to our calculations, divergence between densities of some standard substances calculated by eq 12 and experimental (reference) data in the range of moderate pressures and temperatures does not exceed 1 %, excluding the critical area ($0.95 < T/T_C < 1.1$), $0.6 < \rho/\rho_C < 1.4$). For the so simple equation of state, this result is quite satisfactory. The $P-\rho$ diagram of nitrogen is shown in Figure 5 as the example, and densities calculated by eq 12 are compared there with reference data.[16]

Deviations of densities calculated by eq 12 from data[12,15,16] increase with an approach to the critical point and saturation line. However, in the area of "dense" liquid, divergences of data calculated by eq 12 from reference data[12,15,16] do not exceed experimental errors for the density at pressures of up to 7 to 8 P_C. We should note that coefficients of eq 12 were calculated for the whole array of thermal data obtained in the range from the ideally gaseous state to the liquid density at the line of crystallization. Deviations of densities of liquid carbon dioxide calculated by eq 12 from reference data[12] are shown in Figure 6.

Calculation of Caloric Properties

It is known that the following caloric properties of substances can be calculated by the thermal equation of state with the help of differential equations of thermodynamics: enthalpy, entropy, heat capacity, free energy, etc. However, not every thermal equation of state, which describes thermal data well, allows calculation of caloric properties of substances. According to our calculations, with the help of eq 12 we can calculate some caloric characteristics of a single-component substance with acceptable accuracy, if we know substance functions in the ideally gaseous state, according to the following equations

$$H = H_{ig} + RT(Z - 1) - RT^2 \int_0^\rho \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} \tag{13}$$

$$U = U_{ig} - RT^2 \int_0^\rho \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} \tag{14}$$

$$S = S_{ig} - RT \int_0^\rho \left[Z - 1 + T\left(\frac{\partial Z}{\partial T}\right)_\rho\right] \frac{d\rho}{\rho} \tag{15}$$

$$C_V = C_V^{ig} - RT \int_0^\rho \left[2\left(\frac{\partial Z}{\partial T}\right)_\rho + T\left(\frac{\partial^2 Z}{\partial T^2}\right)_\rho\right] \frac{d\rho}{\rho} \tag{16}$$

$$C_P = C_V + R\left[Z + T\left(\frac{\partial Z}{\partial T}\right)_\rho\right]^2 \left[Z + \rho\left(\frac{\partial Z}{\partial \rho}\right)_T\right]^{-1} \tag{17}$$

Comparison of values of enthalpy, internal energy, entropy, and isobaric heart capacity calculated by eqs 13 to 17 with reference data for argon[15] is shown as an example in Figures 7 to 10. We should emphasize that no caloric data except ideal gas functions were used for calculation of caloric properties of carbon dioxide.

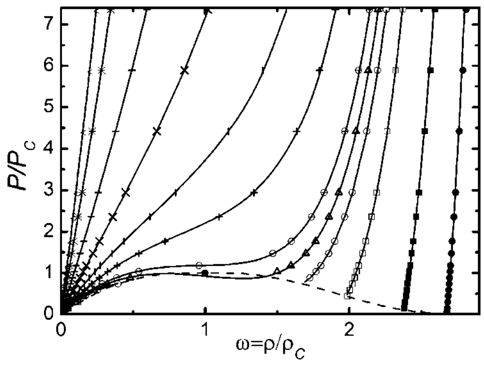

Figure 5. Comparison of values (solid lines) calculated by eq 12 with data of ref 16 on the pressure of nitrogen: ●, T = 70 K; ■, T = 90 K; △, T = 110 K; ○, T = 120 K; Δ, T = 125 K; ⊖, T = 130 K; +, T = 150 K; |, T = 170 K; ×, T = 250 K; −, T = 400 K; ∗, T = 700 K; <, T = 1000 K. Dashed line is line of liquid−vapor equilibria ref 16. ● is critical point.

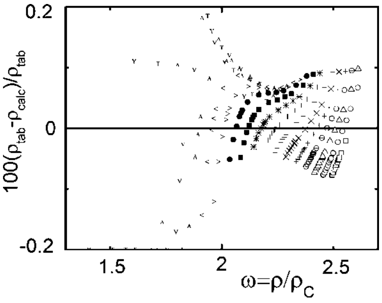

Figure 6. Comparison of densities calculated by eq 12 for the liquid phase of carbon dioxide with data of ref 12: □, T = 220 K; ○, T = 225 K; Δ, T = 230 K; ⊖, T = 235 K; +, T = 240 K; ×, T = 245 K; −, T = 250 K; |, T = 255 K; ∗, T = 260 K; ■, T = 265 K; ●, T = 270 K; >, T = 275 K; <, T = 280 K; A, T = 285 K; V, T = 290 K; Λ, T = 295 K; T, T = 300 K; Y, T = 305 K.

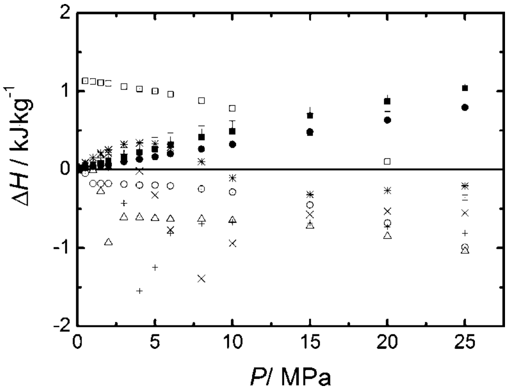

Figure 7. Comparison of argon enthalpy calculated by eq 13 with data of ref 15. $\Delta H = H_{tab} - H_{calc}$: □, T = 90 K; ○, T = 110 K; Δ, T = 130 K; +, T = 150 K; ×, T = 170 K; ∗, T = 200 K; −, T = 250 K; |, T = 300 K; ■, T = 500 K; ●, T = 700 K.

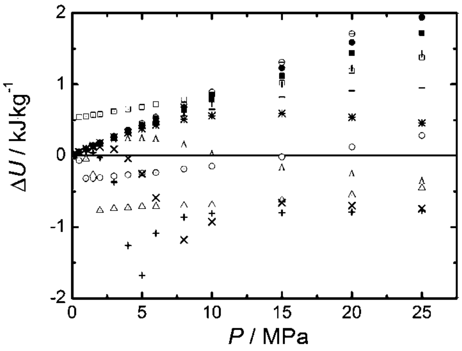

Figure 8. Absolute deviations of values of argon internal energy calculated by eq 14 from data of ref 15. $\Delta U = U_{\text{tab}} - U_{\text{calc}}$: □, $T = 90$ K; ○, $T = 110$ K; Δ, $T = 130$ K; +, $T = 150$ K; ×, $T = 170$ K; ∗, $T = 200$ K; −, $T = 250$ K; |, $T = 300$ K; ■, $T = 400$ K; ●, $T = 500$ K; ⊖, $T = 600$ K; Λ, $T = 700$ K.

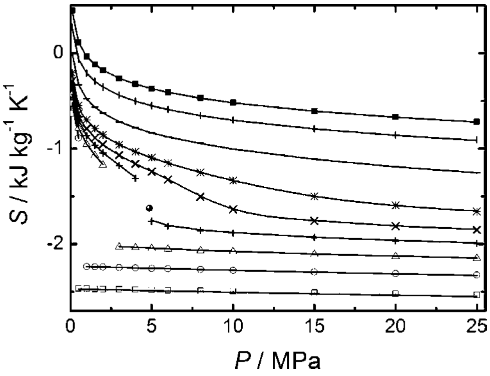

Figure 9. Comparison of argon entropies (lines) calculated by eq 15 with data of ref 15 (symbols). □, $T = 90$ K; ○, $T = 110$ K; Δ, $T = 130$ K; +, $T = 150$ K; ×, $T = 170$ K; ∗, $T = 200$ K; −, $T = 300$ K; |, $T = 500$ K; ■, $T = 700$ K. ● is critical point.

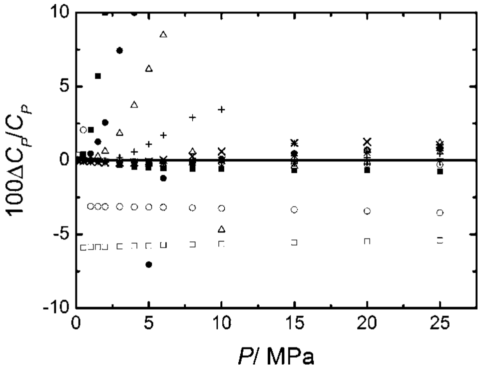

Figure 10. Comparison of argon isobaric heat capacity calculated by eqs 16 and 17 with data of ref 15. $\Delta C_P = C_P^{\text{tab}} - C_P^{\text{calc}}$: □, $T = 90$ K; ○, $T = 110$ K; ■, $T = 130$ K; ●, $T = 150$ K; Δ, $T = 170$ K; +, $T = 200$ K; ×, $T = 250$ K; ∗, $T = 300$ K; −, $T = 400$ K; |, $T = 500$ K; ⊖, $T = 700$ K.

According to calculations of caloric properties of some standard substances, deviations of calculated internal energy, enthalpy, entropy, and isobaric heat capacity from the reference data do not exceed experimental errors. More detailed analysis of this problem is beyond the framework of the current study.

Finally, we should note that the suggested approach has a considerable potential for the following development and specification. With expansion of the range of state parameters, many sought alternative empirical density functions in the equation of state of type 10 will converge because some of them will not meet several physically grounded conditions and restrictions. As for the temperature functions included in eq 2, they can be determined theoretically with the help of potential of intermolecular interactions as it is made in the current paper. Results obtained allow a better understanding of the topology of the thermodynamic surface and reduce the volume of initial experimental information for the correct description of thermodynamic properties of a single-component substance.

Conclusion

A new simple equation of state was developed. This equation contains six coefficients which were fitted to reference data of the compressibility factor of argon, nitrogen, and carbon dioxide. The second virial coefficient was used as the temperature function of the equation. The new equation described the thermal properties and the caloric properties (internal energy, enthalpy, entropy, and isobaric heat capacity) of substances with reasonable accuracy in the range of moderate pressures and temperatures, excluding the critical area. In the area of "dense" liquid, this simple equation gives the density of the substance within experimental errors.

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