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Simple Self-Empirical Equation of State of Liquid and Gas for Engineering Calculations

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ABSTRACT: The new simple semiempirical equation of state (EoS) for the description of $P-\rho-T$ data of "normal" substances was specified. The new EoS has eight individual adjustable coefficients, and it describes the thermal properties of gas, liquid, and fluid with an accuracy within the error of experimental data, except for the critical region. The caloric properties and the speed of sound of argon, nitrogen, and carbon dioxide were calculated with the help of known thermodynamic equations, and in general divergences between calculated and tabular caloric data do not exceed the experimental error. The new equation can be used for engineering calculations at the deficit of experimental data, especially on the caloric properties of substances.

INTRODUCTION

There are many low-parametrical empirical and semiempirical equations of state (EoS) for one-component substances published in literature; however, only some among them are suitable for the description of thermodynamic characteristics of liquid and gas. In detail these equations are analyzed in the remarkable monograph of Reid, Prausnitz, and Sherwood,[1] and some other known publications.[2,3] Most of these equations, including the well-known Benedict−Webb−Rubin (BWR) equation, are modifications of the van der Waals EoS. Most of these equations do not allow the description of thermodynamic properties of substances with fair accuracy, close to the accuracy of the experiment, for the calculation of caloric properties of substances by known $P-\rho-T$ data as well as reliable extrapolation to the little-studied field.

The phenomenological method for deduction of the EoS of liquid and gas is shown.[4] The EoS is written as the sum, where each member is the product of temperature function and density function.[5] It is shown[4] that the second virial coefficient $B(T)$, calculated via the modified stepped potential of intermolecular interaction suggested by the authors, can be used as the temperature function, and the density function can be determined via the analysis of experimental data. Simultaneously, it is necessary to consider the conditions and limitations of the "correct" EoS. The more such limitations and conditions are imposed upon the desired EoS and the stricter their character is, the simpler the semiempirical purposeful search for the EoS of liquid and gas for one-component substance is. In previous works the authors have formulated some additional (except the common known ones) conditions and limitations, which significantly simplify the search for these equations.

1. The preferable structure of the equation,[6] which should be satisfied for all individual substances, was determined. It is shown that the compressibility factor of a one-component substance should include the summand, which is the function of density only. The three-parametrical EoS of liquid and gas was derived in the spirit of van der Waals ideas.
2. It was determined with the help of strict thermodynamic equations[7] that isochoric heat capacity everywhere on the thermodynamic surface is finite and positive, including the spinodal (except the critical point). Some relationships between thermodynamic derivatives on spinodal were determined.
3. The modified stepped potential of intermolecular interaction is suggested.[8] The equations for the second virial coefficient for substances with polar and nonpolar molecules were derived with the help of this potential. These equations describe the second virial coefficient of some substances in the whole range of experimental data.
4. The form of density function in EoS in "elementary functions" is "recovered"[9,10] by the experimental data on thermal properties of real gases of simple substances.[5] The EoS of real gas describing thermodynamic properties of substances was obtained for the densities of up to 1.5 densities at the critical point.[10]
5. The EoS of liquid and gas with the "recovered" form of density function, single for the liquid and gaseous phases,[4] is derived. This equation includes six individual adjustable coefficients and exceeds the most low-parametrical EoS by description accuracy for experimental (tabular) data, including the well-known BWR EoS. The equation takes form:[4]

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

Here $Z = P/\rho RT$ is the compressibility factor, P is pressure, ρ is density, T is the absolute temperature, R is the gas constant of substance, T_c is the critical temperature, ρ_c is the substance

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density at the critical point, ρ_{tr} is density at the triple point, $\tau = T_c/T$ is the reduced reverse temperature, $\omega = \rho/\rho_c$ is the reduced density, $\omega_{tr} = \rho_{tr}/\rho_c$ is the reduced density at the triple point, and a_1 to a_6 are adjustable coefficients.

The EoS1 is satisfied for some substances[4] at densities from the ideal gas to the triple point in the range of temperatures of up to (5 to 7) T_C and pressures of up to (5 to 10) P_C. However, this equation has some essential disadvantages. Among the main ones are considerable divergence between calculated and tabular values of thermodynamic parameters in the gas and critical area and significant deviations of calculated values of isochoric heat capacity and speed of sound from the experimental data.

EQUATION OF STATE OF LIQUID AND GAS FOR ENGINEERING CALCULATIONS

The current work is aimed at the derivation of low-parametrical physically grounded united EoS for liquid and gas, which could describe thermodynamic properties of a one-component substance with an error, slightly exceeding the experimental error and being significantly better than other known low-parametrical single EoS. This equation derived in the framework of phenomenological approach[4] should describe experimental thermodynamic data, perform reliable extrapolation to the little-studied field, and calculate caloric data, including isochoric heat capacity and speed of sound of substance, much better than eq 1 without use of experimental data on the above properties.

As it was already mentioned, the temperature functions in EoS were obtained with the help of the modified stepped potential of intermolecular interaction.[4] The number of steps in this potential was chosen to describe the second virial coefficient of nonpolar and polar gases in the limits of initial errors. For this purpose it was necessary and sufficient to keep the minimal number of steps in the potential. The stepped potential[4] is the superposition of the hard sphere potential, one potential barrier, one potential well, and London potential.

With a rise of requirements to accuracy of description of initial experimental or tabular $P-\rho-T$ data and expansion of the range of state parameters, the number of steps in approximating potential required for the derivation of "qualitative" EoS can increase. However, it is not obvious that the unlimited formal increase in the number of steps in approximating the potential will obligatorily lead to the improvement of EoS quality. Thus, an increase in the number of steps in the temperature functions and, hence, an increase in the number of temperature functions can impede the empirical search for density functions in EoS in "elementary" functions.[5]

In the current work we have confined ourselves to adding to the approximating potential of one more step as compared with eq 1 in the zone of repulsion.[4] Moreover, it was taken as before[10] that because of a high slope of potential the width of a barrier is very low and not more than one molecule can simultaneously be near the given particle. In this case, we can assume that the form of this potential contribution into the compressibility factor will be the same as in rarefied gas. Then the additional summand in 1 for the compressibility factor can be written as

$$c\omega(e^{-b\tau} - 1) \tag{2}$$

Therefore, the modified interaction potential is the superposition of two repulsion potentials in the form of rectangular barriers with different heights, a rectangular potential well, and London potential.

It is known that maximal divergences between data calculated by different semiempirical equations and experimental (tabular) ones occur in the critical area and at the line of liquid–vapor saturation. These divergences occurred even after the supplement of EoS 1 with summands 2. These divergences relate to the complexity of description of the thermodynamic properties of substances in the critical area. Behavior features of these properties are caused by fluctuation effects related to the infinite compressibility of substance at the critical point, and they do not depend on the specific form of potential of intermolecular interaction. In our opinion, the contribution of fluctuation effects to the EoS should be taken into account already in the regular part of the EoS. The introduction of a corresponding summand into the EoS should provide a better agreement between calculated and experimental data in the critical area and improve the description of thermodynamic data at the line of saturation. It is evident that this approach cannot lead particularly to the manifestation of singularity of isochoric heat capacity at the critical point.

An attempt to take into account the effect of critical fluctuations on the EoS was made previously[11] at the description of thermodynamic properties of helium-4. An additional empirical summand in the EoS of helium[11] allowed both significant improvement in the description quality of initial data in the critical area and reliable extrapolation from the low-temperature zone to the high-temperature one more than by 1000 temperature ranges. However, for some other substances, in particular, nitrogen and carbon dioxide, this correction of the initial EoS did not lead to satisfactory results.

In this connection to improve the description of thermal and caloric data in the critical area, EoS 1 was supplemented with the empirical summand of the following type

$$c(e^{6\tau} - 1 - 6\tau)(\omega_{tr} - \omega)^3(3\omega - \omega_{tr})\omega^2 \tag{3}$$

Considering the above, the simple EoS of liquid, gas, and fluid after corresponding transformations can be written as

$$\begin{aligned} Z = {} & 1 + a_1(e^{\tau} - 1 - \tau)(\omega_{tr} - \omega)^2(4\omega - \omega_{tr})\omega \\ & + a_2(e^{6\tau} - 1 - 6\tau)(\omega_{tr} - \omega)^3(3\omega - \omega_{tr})\omega^2 - \\ & - a_3\omega(e^{-\tau} - 1) - a_4\omega\tau - a_5\omega(e^{-\tau_B\tau} - 1) + \frac{a_6\omega}{1 - a_8\omega} \\ & + \frac{a_7\omega^3}{(1 - a_8\omega)^3} \end{aligned} \tag{4}$$

It is taken into account in eq 4 that for the optimal description of thermodynamic properties of some substances parameter b in the exponent of 2 is close to Boyle reduced reverse temperature $\tau_B = T_B/T$.

Equation 4 includes eight empirical adjustable parameters and physical characteristics of the studied substance: critical temperature T_C, Boyle temperature T_B, and density of substance at critical ρ_C and triple ρ_{tr} points.

COMPARISON WITH EXPERIMENTAL AND TABULAR DATA ON THERMAL PROPERTIES OF SUBSTANCES

The new EoS 4 was checked on substances with agreed experimental data and basic "fundamental" EoS. According to our calculations, eq 4 described qualitatively the thermodynamic surface and thermal properties of normal substances with the error, close to the error of experimental (tabular) data.

Table 1. Coefficients of Equation 4 and Parameters in Critical Point (ρ_c, T_c) and $\omega_{tr} = \rho_{tr}/\rho_c$ Reduced Density in the Triple Point for Argon, Nitrogen, and Carbon Dioxide

substance	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8	ω_{tr}	ρ_C / $\mathrm{kg \cdot m^{-3}}$	T_C / K	τ_B
argon[12]	0.016802	1.0739×10^{-5}	0.446515	1.854836	0.230806	0.399972	−0.000167	0.322080	2.645202	535.6	150.687	2.70601
nitrogen[13]	0.016240	4.6734×10^{-6}	0.592235	1.982467	0.250060	0.463329	0.013406	0.217982	2.768023	313.3	126.192	2.57544
carbon dioxide[14]	0.021826	3.5569×10^{-5}	1.560635	2.620626	0.211978	0.485738	0.031188	0.169628	2.520381	467.6	304.128	2.30166

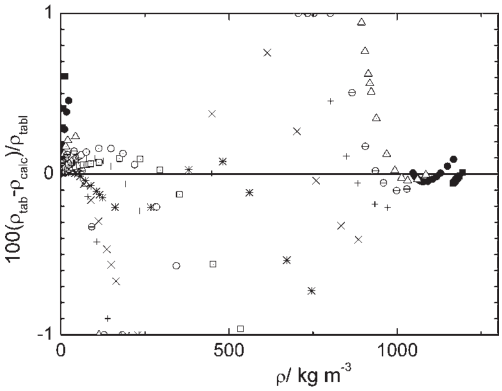

Figure 1. Deviation of carbon dioxide densities calculated by eq 4 from the tabular data of ref 14: ■, T = 220 K; ●, T = 250 K; ◬, T = 280 K; ⊖, T = 300 K; +, T = 320 K; ×, T = 350 K; ∗, T = 400 K; ⊡, T = 500 K; ⊙, T = 700 K; |, T = 1000 K.

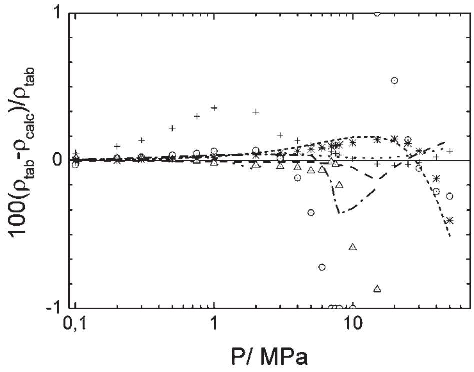

Figure 2. Deviation of carbon dioxide densities calculated by eq 4 from tabular data of ref 14: +, T = 260 K; ⊙, T = 325 K; ◬, T = 430 K; ∗, T = 800 K; lines are deviation of densities calculated by technical equation of ref 15: · · ·, T = 260 K; − − −, T = 325 K; − · −, T = 430 K; ---, T = 800 K.

Adjustable coefficients of eq 4 for some "normal" substances were determined by the minimization of deviations of the calculated compressibility factor from the tabular data by the least-squares method $\sigma = ((\sum(Z_{tab} - Z_{calc})^2)/N)^{1/2}$. Coefficients of eq 4 for argon,[12] nitrogen,[13] and carbon dioxide[14] are shown in Table 1; some physical characteristics are also shown there. Densities of these substances at given temperatures and pressures were calculated, using individual coefficients determined by eq 4. Average relative deviations of calculated densities of these substances from the tabular data in the range from 0 to the density at the line of melting AAD are as follows: for argon it is 0.2 % at the temperatures of up to 700 K and pressures of up to 25 MPa; for nitrogen it is 0.2 % at the temperatures of up to 1250 K and pressures of up to 25 MPa; and for carbon dioxide it is 0.25 % at the temperatures of up to 1100 K and pressures of up to 50 MPa. It is necessary to emphasize that deviations of densities calculated by eq 4 from tabular values[12−14] do not exceed divergences between experimental data of different authors. Results shown in the table prove the fact that eq 4 meets the requirements made to equations for engineering calculations.[15]

Here we will discuss in detail only the calculation of thermodynamic properties of carbon dioxide[14] by the suggested eq 4 because of the lack of space.

Results of the comparison of carbon dioxide densities calculated by eq 4 with tabular data[14] at the given temperature and pressure are shown in Figure 1. According to the figure, divergences between these data do not mainly exceed (0.2 to 0.3) %. Despite that the deviation of densities calculated by eq 4 from tabular data[14] increases in the critical area, the compressibility factor at the critical point calculated by the whole data array agrees satisfactorily with the experimental value. Thus, the compressibility factor at the critical point by eq 4 equals Z_c^{calc} = 0.27347, and experimental value is Z_c^{exp} = 0.27459;[14] the pressure calculated by eq 4 equals P_c^{calc} = 7.3472, and according to experimental data[14] P_c^{exp} = 7.3773.

In Figure 2 the eight-parametrical eq 4 is compared with a twelve-parametrical equation for technical applications.[15] This technical equation[15] is polynomial by temperature and density degrees with fractional indices. According to Figure 2, eq 4 can be compared with technical EoS[15] by the accuracy of description for tabular data.[14]

■ CALCULATION OF CALORIC PROPERTIES

It is known that the following caloric properties of substances can be calculated by thermal EoS with the help of differential equations of thermodynamics: enthalpy, entropy, and isochoric and isobaric heat capacities as well as the speed of sound. However, not every thermal EoS, even an equation which describes thermal data well, allows the calculation of the caloric properties of substances with acceptable accuracy because operations of differentiation and integration are required for that. According to our calculations, by means of eq 4 we can calculate some caloric characteristics of the one-component substance with acceptable accuracy, if we know the caloric properties in the ideal-gaseous state.

The caloric properties of carbon dioxide are calculated with the help of the known thermodynamic relationships:

$$H = H_{ig} + RT(Z-1) - RT^2 \int_0^{\rho} \left(\frac{\partial Z}{\partial T}\right)_{\rho} \frac{d\rho}{\rho} \qquad (5)$$

$$U = U_{ig} - RT^2 \int_0^{\rho} \left(\frac{\partial Z}{\partial T}\right)_{\rho} \frac{d\rho}{\rho} \qquad (6)$$

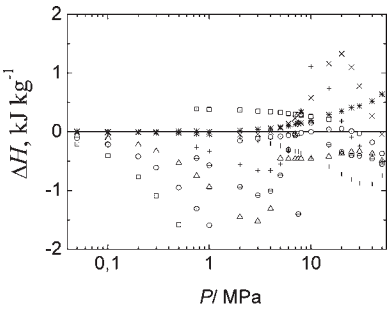

Figure 3. Deviation of carbon dioxide enthalpy calculated by eq 5 from tabular data of ref 14: $\Delta H = H_{\text{tab}} - H_{\text{calc}}$: ⊡, T = 220 K; ⊙, T = 250 K; ◬, T = 280 K; ⊖, T = 305 K; +, T = 350 K; ×, T = 400 K; ∗, T = 600 K; |, T = 1000 K.

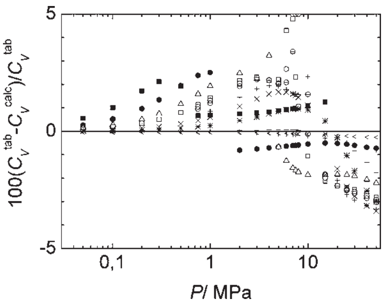

Figure 4. Deviation of isochoric heat capacity of carbon dioxide calculated by eq 7 from tabular data of ref 14: ■, T = 220 K; ●, T = 250 K; ◬, T = 280 K; ⊡, T = 300 K; ⊙, T = 305 K; ⊖, T = 310 K; +, T = 330 K; ×, T = 350 K; ∗, T = 400 K; —, T = 500 K; |, T = 700 K; <, T = 1000 K.

$$C_V = C_V^{\text{ig}} - RT\int_0^\rho \left[2\left(\frac{\partial Z}{\partial T}\right)_\rho + T\left(\frac{\partial^2 Z}{\partial T^2}\right)_\rho\right]\frac{d\rho}{\rho} \qquad (7)$$

$$C_P = C_V + R\left[Z + T\left(\frac{\partial Z}{\partial T}\right)_\rho\right]^2 \cdot \left[Z + \rho\left(\frac{\partial Z}{\partial \rho}\right)_T\right]^{-1} \qquad (8)$$

$$w = \sqrt{RT\left(\frac{R}{C_V}\left[Z + T\left(\frac{\partial Z}{\partial T}\right)_\rho\right]^2 + \left[Z + \rho\left(\frac{\partial Z}{\partial \rho}\right)_T\right]\right)} \qquad (9)$$

In eqs 5 to 9 the compressibility factor Z is determined by eq 4.

Below, the caloric characteristics of carbon dioxide calculated by eqs 4 to 9 are compared with tabular data[14] and the technical EoS.[15] We should note that the technical equation,[15] as the "reference" EoS,[14] was obtained via the combined processing of different (caloric and thermal) experimental data, whereas the caloric properties in the current work were calculated without use of any caloric data except for the enthalpy and heat capacity of ideal gas.

The calculated values of enthalpy and isochoric heat capacity are compared with tabular data[14] in Figures 3 and 4 as examples. According to these figures and analysis of experimental data,[14] the deviation of enthalpy and isochoric heat capacity calculated by eqs 4, 5, and 7 from tabular data[14] does not exceed the experimental error for these characteristics.

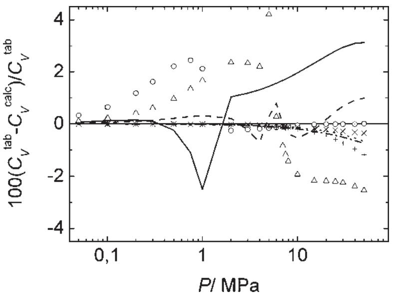

Figure 5. Deviation of carbon dioxide isochoric heat capacity calculated by eq 7 from tabular data of ref 14: ⊙, T = 240 K; ◬, T = 290 K; +, T = 500 K; ×, T = 900 K; lines are deviation of isochoric heat capacity calculated technical equation of ref 15: —, T = 240 K; – – –, T = 290 K; · · ·, T = 500 K; —·—·—, T = 900 K.

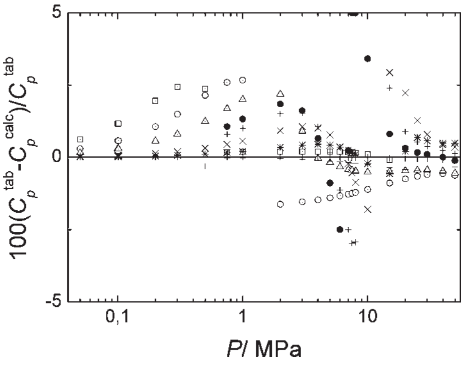

Figure 6. Deviation of carbon dioxide isobaric heat capacity calculated by eq 8 from tabular data of ref 14: ⊡, T = 220 K; ⊙, T = 250 K; ◬, T = 280 K; ●, T = 305 K; +, T = 325 K; ×, T = 350 K; ∗, T = 400 K; —, T = 600 K; |, T = 1000 K.

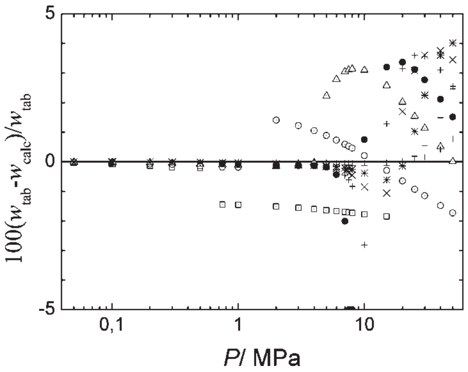

Figure 7. Deviation of speeds of sound in carbon dioxide calculated by eq 8 from tabular data of ref 14: ⊡, T = 220 K; ⊙, T = 250 K; ◬, T = 280 K; ●, T = 305 K; +, T = 325 K; ×, T = 350 K; ∗, T = 400 K; —, T = 600 K; |, T = 1000 K.

Calculations of isochoric heat capacity calculated by eqs 4 and 7 and engineering equation[15] are compared in Figure 5 with tabular data.[14] According to the figure, by the accuracy of description of tabular data,[14] the equations in the current study yield slightly to the equation for technical calculations.[15]

We have obtained similar results from the comparison of calculations on isobaric heat capacity and speed of sound (Figures 6 to8) with tabular data[14] and the technical equation.[15] The deviation of calculated values from tabular ones[14] does not

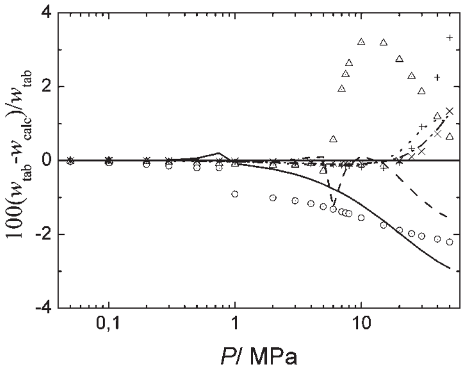

Figure 8. Deviations of speeds of sound in carbon dioxide calculated by eq 8 from tabular data of ref 14: ⊙, T = 230 K; △, T = 270 K; +, T = 450 K; ×, T = 800 K; lines are speeds of sound calculated by technical equation of ref 15: —, T = 230 K; — — — △, T = 270 K; · · ·, T = 450 K; —·—·—, T = 800 K.

exceed the experimental error at heat capacity measurement (Figure 6). Despite that deviations of calculated speed of sound in carbon dioxide from those presented in ref 14 exceed the experimental error on speed of sound measurement (Figure 7), the description accuracy for data on the speed of sound by eqs 4 and 9 does not yield (Figure 8) to the engineering equation.[15]

■ CONCLUSIONS

In the framework of phenomenological approach developed previously (e.g., see ref 4), the EoS for the description of $P-\rho-T$ data of "normal" substances was specified. Equation 1 was supplemented with two summands, which take into account intermolecular repulsion at small distances and behavior features of thermodynamic properties of substances in the critical area. The obtained EoS 4 describes the thermal properties of gas, liquid, and fluid within the error of experimental data, and it is comparable by the accuracy of description with the technical equation.[15]

The caloric properties of some substances were calculated with the help of known thermodynamic equations with the use of eq 4. Divergences between calculated and tabular caloric data[12−14] do not exceed the experimental error (except the speed of sound). By the accuracy of description of the caloric data, the suggested equation does not yield to the technical equation.[15]

In our opinion, eq 4 can be used for engineering calculations at the deficit of experimental data, especially on the caloric properties of substances. We should emphasize that for calculation of caloric properties of normal substances we have not used any caloric data, except for functions of ideal gas, whereas the technical equation[15] and a fortiori all equations for calculation of standard reference data were obtained as the result of combined processing of caloric and thermal data and speed of sound.

The results obtained allow better understanding of topology of thermodynamic surface and significant decrease in the scope of initial experimental information for correct description of thermodynamic properties of one-component substance.

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