Equation of liquid, gas, and fluid state for methane

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Abstract. Using methods and approaches, previously developed by the authors, a new fundamental low-parametric equation of state for methane (in the form of the reduced Helmholtz function) has obtained to describe the thermodynamic properties. It allows describing the thermal properties of gas, liquid, and fluid at pressures of up to 20 MPa with sufficiently high accuracy close to the experimental one (with the exception of the critical region). The sound speed and caloric properties of methane have been calculated without involving any caloric data, with the exception of ideal gas enthalpy. The values of speed of sound, isochoric heat capacity, and other thermodynamic properties obtained by calculations are in good agreement with the experimental data.

1. Introduction

Methane is a main element of natural gas. In this regard, knowledge of the thermal and caloric properties of methane is necessary to liquefy, separate, store, pump and transport natural gas. In addition methane is used for the production of hydrogen, alcohols and many other products of the chemical industry. In view of the growing efforts to optimize chemical production, it is necessary to ensure the accurate thermodynamic properties of methane. In addition, since methane is the main component of natural gas, the methane properties are the key data for the development, optimization of the equation of state for natural gas.

Knowledge of thermodynamic properties is necessary to create new technologies; therefore, such studies are currently carried out with pure substances both in liquid and gaseous states, see, for example, [1, 2]. It is known that in equations of state used to obtain reference tables on the thermodynamic properties of single-component substances, the number of fitting constants reaches 40–100 or more. To obtain fitting constants in such equations of state, almost all experimental data on the thermal and caloric properties of a substance are used as initial data. Based on experimental data on the methane properties, a fundamental equation for the Helmholtz energy (40 adjustable constants and 96 different exponents), which describes the thermodynamic properties in the temperature range from 90 K to 625 K at pressures of up to 1000 MPa, has been developed [3]. Comparison of calculated $P\cdot\rho\cdot T$ data with experimental data shows that deviations are within $\pm 0.03\%$ for the pressures below 12 MPa and temperatures below 350 K and from $\pm 0.03\%$ to $\pm 0.15\%$ for higher pressures and temperatures. For the speed of sound, the error ranges from $\pm 0.03\%$ to $\pm 0.3\%$ depending on temperature and pressure. The calculated values of heat capacity ($C_p$ and $C_v$) are estimated with an accuracy of $\pm 1\%$ [3].

A new class of technical equations of state for non-polar and weakly polar liquids and typical polar liquids was developed in [4-5]. This model has a low number of adjustable parameters (12 polynomial and exponential terms). The equation allows describing thermal properties of
methane with sufficient accuracy (from ±0.2% to ±0.5% by density at a pressure above 30 MPa, 1-2% by sound speed, and 2% by heat capacity).

2. Fundamental low-parametric equation of state for methane

Physically substantiated semi-empirical unified equations of state for gas, liquid, and fluid were derived in [6–13] earlier by the authors to describe the thermodynamic properties of “normal” substances (argon, xenon, nitrogen, carbon dioxide, oxygen, hexafluoride sulfur, etc.). The best form to describe of the compressibility factor \( Z = PV/RT \) was established by analyzing the differential equations of thermodynamics. It was clearly shown that the compressibility factor should contain only the density function as one of the terms.

In the developed equations of state [7–13], it is possible to fulfill strictly the classical critical conditions with almost no loss of accuracy in the description of the initial data. The number of empirical fitting coefficients of these equations usually does not exceed 9 - 12. These equations make it possible to calculate with satisfactory accuracy the thermal and caloric characteristics of “normal substances” (excluding the vicinity of the critical point) at temperatures and pressures exceeding the critical parameters 2-5 and 5-7 times, respectively.

Now, it is customary to represent the thermodynamic properties of a substance using the fundamental equations of state, which are expressed in form of the reduced Helmholtz function \( \alpha \) with independent variables of density \( \rho \) and temperature \( T \)

\[
\alpha = \alpha^0 + \alpha' = F/RT = \varphi(T, \rho). \tag{1}
\]

Here \( \alpha^0 \) is the reduced Helmholtz function of an ideal gas, \( \alpha' \) is the reduced residual Helmholtz function, \( F \) is the free Helmholtz energy, and \( R \) is the gas constant. The equation of state (1) has certain advantages as compared to the ES for compressibility factor \( Z \). Since mainly the differentiation procedure is used to calculate the physical property of a single-component substance by (1), whereas when calculating these properties with the help of the compressibility factor, it is often necessary to use the integration procedure, which cannot be always performed.

Compressibility factor \( Z \) (\( P \) is pressure) is related to the reduced Helmholtz function \( \alpha' \) by the known relation

\[
Z(\rho, T) = 1 + \rho \left( \frac{\partial \alpha'(\rho, T)}{\partial \rho} \right)_r = 1 + \rho \left( \frac{\partial \alpha'\omega(\rho, \tau)}{\partial \omega} \right)_\tau \tag{2}
\]

Here \( \tau = T_c/T \) is the reduced inverse temperature, \( T_c \) is the critical temperature, \( \omega = \rho/\rho_c \) is the reduced density, and \( \rho_c \) is the density of substance at a critical point. The equation for the reduced residual Helmholtz function \( \alpha' \) can be found using (2), if the equation for \( Z \) is known.

It is shown in [6, 11] that the equations for the compressibility factor \( Z \) and for the reduced Helmholtz function should contain only the density function as one of the terms, that is

\[
Z(T, \rho) = 1 + f_1(T, \rho) + f_2(\rho) \tag{3}
\]

\[
\alpha(T, \rho) = \alpha'(T, \rho) + \lambda(T, \rho) + \psi(\rho). \tag{4}
\]

The expression for the density-only function from the equation for the compressibility factor is presented in [11]. When integrating formula (2), a very complex expression for \( \psi(\rho) \) in (4) is obtained, and therefore a new approximation equation for this function is proposed in [13] in relation (4).

The fundamental reduced low-parametric equation of state obtained in [13] for reliable description of the thermal and caloric properties of normal single-component substances in liquid, gas, and fluid states (except for the vicinity of the liquid – vapor critical point) in the above variables has the form:
\[ \alpha'(\omega, \tau) = a_1(e^{\tau} - 1 - \tau)e^{-\frac{\omega}{1-Z_C \omega}} + a_2 \omega \tau + a_3(e^{-\tau} - 1)\omega + a_4(e^{-3\tau} - 1)\omega + a_5(e^{6\tau} - 6\tau)\omega^2 e^{-\frac{5Z_C \omega}{1-Z_C \omega}} + a_6(e^{3\tau} - 1 - 3\tau)e^{-\frac{2\omega}{1-Z_C \omega}} + a_7 \ln(1 - Z_C \omega) + \frac{a_8 \omega}{1-Z_C \omega} + \frac{a_9 \omega^2}{(1-Z_C \omega)^2} + a_{10} e^{-\omega}. \] (5)

Here, it is taken into account that according to the Filippov – Timmermans rule, \( \rho_C / \rho_0 = Z_C \), where \( \rho_0 \) is the density of liquid supercooled to absolute zero, and the expression in the density functions in (5) is

\[ \frac{\omega}{1-Z_C \omega} = \frac{V_C}{V-V_0}. \]

The equation for calculation of coefficients in (1) and (5) takes form:

\[ P = \rho RT \left( 1 + \omega \left( \frac{\partial \alpha'}{\partial \omega} \right)_T \right) \] (6)

Equations (5) and (6) contain 10 empirical fitting coefficients. The adjustable factors included in (5) and (6) were found by minimizing the deviations between the data calculated by (6) and the initial (tabular or experimental) data on pressure, for example, by the least squares method. After finding the coefficients of the desired equation (5), the density values at a given temperature and pressure are calculated from equation (6) by a numerical method. When three critical conditions are met, the number of fitting empirical coefficients decreases to 7, and 4 of them are necessary to describe the density-only function (coefficients \( a_7 - a_{10} \)) in equation (5).

### 3. Comparison with experiment and tabular data

To calculate \( \alpha' \), we used an equation derived from the correlation of the equation for isobaric heat capacity in the ideal gas state [3].

The coefficients of equation (5) for methane are shown in table 1. The critical parameters of methane are also given there, as well as the mean square \( \sigma \) and weighted average AAD deviations of the calculated density values from the tabular data [3] in the temperature range of up to 600 K and pressures of up to 20 MPa.

**Table 1.** Coefficients \( a_1-a_{10} \) for calculation according to (5) and (6); critical parameters; \( \sigma \), AAD.

| Parameters | Value           |
|------------|-----------------|
| \( a_1 \)  | 28.38516×10^{-3} |
| \( a_2 \)  | -1.967673       |
| \( a_3 \)  | -0.61124358     |
| \( a_4 \)  | 8.374763×10^{-3} |
| \( a_5 \)  | -7.753397×10^{-4} |
| \( a_6 \)  | -3.075999×10^{-2} |
| \( a_7 \)  | -1.666971       |
| \( a_8 \)  | 2.759766×10^{-2} |
| \( a_9 \)  | 2.098114×10^{-4} |
| \( a_{10} \)| -1.57829×10^{-3}  |
| \( Z_C \)  | 0.285853        |
| \( T_C \)  | 190.564         |
The results of comparing methane density values calculated by (5) and (6) with the “reference” tabular data [3] at a given temperature and pressure are presented in figure 1. As it can be seen from the figure 1, the deviation between the tabular data of [3] and those calculated in this paper do not exceed 0.3 - 0.5%. The results given in figure 1 indicate that equation (5) meets the requirements for the equations of state for engineering calculations (see [5]).

![Figure 1](image)

**Figure 1.** Deviation of density values, calculated according to (5) and (6) from tabular data [3] for full pressure range.

The caloric properties of methane were also calculated from the state equation (5) using the differential equations of thermodynamics. We would like to note that for the calculation of the fitting coefficients in equation (5), only $P-\rho-T$ data were used as the initial ones, and not a set of dissimilar caloric and thermal properties of the substance.

Our calculations showed that the caloric characteristics can be calculated with acceptable accuracy using equation (5) and the properties of the substance in the ideal gas state [3].

The calculations of the caloric properties of methane have show that the values of caloric properties and sound speed calculated by equations (5), (6) are consistent with the tabular data mainly within the estimated error of tabular and experimental data of [3-5, 14-17], with the exception of the near-critical region.

When calculating the speed of sound in methane, no experimental data on the sound speed and caloric properties of substances are used as initial data, excluding the caloric properties in an ideal gas state.

The calculated values of the sound speed are compared with the experimental data obtained in [14–17] in Figures 2 and 3. It can be seen from the figures that the calculated values of the sound speed are in satisfactory agreement with the experimental data in a wide range of temperatures and pressures in gas, liquid, and fluid.
Figure 2. Comparison of calculated speed of sound $W$ in methane (line) with tabular data from [3] (points) for isotherms depending on pressure.

The discrepancies between these data in the gas region (figure 3) do not exceed 0.3–0.5% and increase substantially in the critical region, especially when approaching the saturation line from the liquid phase side. However, experimental errors in measuring the sound speed also increase significantly in this area (see [3, 14–17]).

Figure 3. Deviation of the experimental speed of sound values in CH$_4$ from those calculated for isotherms of 150, 170, 240, 300, 350, and 375 K. (1) Data from [14]; (2) data from [15]; (3) data from [16]; (4) data from [17].

The isochoric and isobaric heat capacities of CH$_4$ are insufficiently studied characteristics. In Figure 4 we compare the results of calculations of isochoric heat capacity of methane is compared with experimental data of [18–19]. The experimental data on $C_V$ are not used in calculation by equation (5). As it can be seen from Figure 4, the deviations of calculated isochoric heat capacity from the experimental data of [18–19] do not basically exceed the experimental errors.
Figure 4. Deviation of experimental data on the isochoric heat capacity of CH$_4$ from the calculated values $\delta C_V, \% = 100(C_{Vexp}/C_{Vcalc})/C_{Vcalc}$ for isochores. (1) Data from [18]; (2) data from [19].

Conclusions
Equation of state (5) was developed to describe the thermal properties of methane. In this paper, we have presented the calculation results on some thermodynamic characteristics of methane. Equation (5) describes the thermal properties of gas, liquid, and fluid mainly within the experimental error at pressures of up to 20 MPa. The discrepancies between calculated and tabular [3] caloric data (in particular, regarding the speed of sound and isochoric heat capacity) generally do not exceed the experimental errors.

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