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Special Equations of State for Methane, Argon, and Nitrogen for the Temperature Range from 270 to 350 K at Pressures up to 30 MPa[1]

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In order to describe the thermodynamic behavior of methane, argon, and nitrogen in the so-called "natural-gas region," namely, from 270 to 350 K at pressures up to 30 MPa as accurate as possible with equations of a very simple form, new equations of state for these three substances have been developed. These equations are in the form of a fundamental equation in the dimensionless Helmholtz energy; for calculating the pressure or the density, the corresponding equations explicit in pressure are also given. The residual parts of the Helmholtz function representing the behavior of the real gas contain 12 fitted coefficients for methane, 8 for argon, and 7 for nitrogen. The thermodynamic relations between the Helmholtz energy and the most important thermodynamic properties and the needed derivatives of the equations are explicitly given; to assist the user there is also a table with values for computer-program verification. The uncertainties when calculating the density ρ, the speed of sound w, the isobaric specific heat capacity c_p, and the isochoric specific heat capacity c_v are estimated as follows. For all three substances it is $\Delta\rho/\rho \leqslant \pm 0.02\%$ for $p \leqslant 12$ MPa and $\Delta\rho/\rho \leqslant \pm 0.05\%$ for higher pressures. For methane it is $\Delta w/w \leqslant \pm 0.02\%$ for $p \leqslant 10$ MPa and $\Delta w/w \leqslant \pm 0.1\%$ for higher pressures; for argon it is $\Delta w/w \leqslant \pm 0.1\%$ for $p \leqslant 7$ MPa, $\Delta w/w \leqslant \pm 0.3\%$ for $7 < p \leqslant 30$ MPa; and for nitrogen it is $\Delta w/w \leqslant \pm 0.1\%$ for $p \leqslant 1.5$ MPa and $\Delta w/w \leqslant \pm 0.5\%$ for higher pressures. For all three substances it is $\Delta c_p/c_p \leqslant \pm 1\%$ and $\Delta c_v/c_v \leqslant \pm 1\%$ in the entire range.

KEY WORDS: argon; caloric properties; density; equation of state; Helmholtz function; methane; nitrogen.

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1. INTRODUCTION

EUROMET is a European collaboration in measurement standards that was established in 1987. The members of EUROMET are the national metrology institutes from the States of the European Communities (EC), the States of the European Free Trade Association (EFTA), and the Commission of the European Communities. EUROMET projects are collaboration projects on subjects of interest. These projects are divided into relevant subject fields, one of which is called flow measurement. One of the main aims in this field is to improve the measurement services. In the field of flow measurement of, in particular, fluids in the gas phase, EUROMET is currently involved in several projects including the EUROMET Project No. 202, "Gas Density."

The overall objective of the EUROMET project "Gas Density" is to improve the uncertainty of the determination of gas density, which is an important parameter in the determination of mass flow. As mass flow forms the basis for accountancy of gas, the improvement of gas density determination will improve the premises for custody transfer. One of the scientific and technical objectives is to undertake measurements of density of the highest accuracy (with an uncertainty of less than or equal to ±0.02%) for selected pure gases and gas mixtures and to develop formulations and tables for the representation of the density and the caloric properties of these gases.

The measurements and the formulations should cover a selected temperature and pressure range (0 to 70°C, 0 to 30 MPa) relevant to the needs of custody transfer, the calibration of mass flow meters, and the calibration of industrial densitometers. One principle objective is to obtain international acceptance of the final correlations, for example, via IUPAC (International Union of Pure and Applied Chemistry) and CEN (Comité Européen de Normalisation).

In this framework it is the purpose of this paper to present equations of state for the first three substances, methane, argon, and nitrogen, for which sufficiently accurate density measurements have already been performed, at least in the pressure range $p \leqslant 12$ MPa. Since, however, the pressure range $12 < p \leqslant 30$ MPa has been covered only by density measurements of an average uncertainty of less than ±0.05% and since there is a lack of sufficiently accurate caloric data in the entire region (with the exception of the speed of sound of methane), the equations have to be considered to be preliminary ones in this respect.

2. GENERAL FORM AND REQUIREMENTS OF THE NEW EQUATIONS OF STATE

2.1. Requirements of and Basis for the New Equations

Based on the field of application mentioned in Section 1, the new short equations of state for methane, argon, and nitrogen should cover a temperature range from 0 to 70°C (273 to 343 K) at pressures up to 30 MPa. In this region the final equations should have an uncertainty in the density ρ of $\Delta\rho/\rho \leqslant \pm 0.02\,\%$, and with regard to the caloric properties it would be desirable to achieve uncertainties in the speed of sound w, in the isobaric specific heat capacity c_p, and in the isochoric specific heat capacity c_v of $\Delta w/w \leqslant \pm 0.1\,\%$, $\Delta c_p/c_p \leqslant \pm 0.5\,\%$, and $\Delta c_v/c_v \leqslant 0.5\,\%$. Since, however, at present the experimental data of these properties do not have such small uncertainties (with the exception of the density for $p \leqslant 12$ MPa and the speed of sound at lower pressures), the new equations should be as accurate as possible. This means that the uncertainty in these properties, which are the most important ones for the applications considered here, should correspond to the uncertainty of the most accurate experimental data. These requirements should be met with equations of state which are as simple and short as possible.

As precondition for the equations to meet the uncertainty requirements, the best experimental data of ρ, w, c_p, and c_v, which cover at least partly the range of validity of the equations, have been selected; the information on the single data sets is given in Sections 3.1 to 3.3. These data were used either to develop the equations or to compare them with the corresponding values calculated from the equation. For this purpose, the temperature values of all these data were converted to temperatures based on the "International Temperature Scale of 1990 (ITS-90)" [1]. Thus, the new equations for methane, argon, and nitrogen correspond to the ITS-90.

2.2. General Form of the New Equations

The new equations of state for CH_4, Ar, and N_2 are fundamental equations expressed in the form of the Helmholtz energy A with the two independent variables, density ρ and absolute temperature T. The dimensionless Helmholtz energy $\Phi = A/(RT)$ is split into a part depending on the ideal gas behavior Φ° and a part which takes into account the residual fluid behavior Φ^{r}, namely,[3]

$$\Phi(\delta, \tau) = \Phi^{0}(\delta, \tau) + \Phi^{r}(\delta, \tau) \tag{1}$$

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[3] Definitions of symbols are given under Nomenclature.

Table I. Physical Constants Used for CH_4, Ar, and N_2

Property	CH_4		Ar		N_2	
Molar mass M ($g \cdot mol^{-1}$)	16.0428	[2]	39.948	[2]	28.01348	[2]
Specific gas constant R ($J \cdot kg^{-1} \cdot K^{-1}$)[a]	518.2705		208.1333		296.8039	
Critical temperature T_c (K)[b]	190.564	[3]	150.687	[4]	126.2054	[5]
Critical density ρ_c ($kg \cdot m^{-3}$)	162.66	[3]	535.6	[4]	313.1058	[5]

[a] $R = R_m/M$, where R_m is the molar (universal) gas constant with $R_m = 8.31451\ J \cdot mol^{-1} \cdot K^{-1}$ [6].

[b] The values of the critical temperature correspond to the ITS-90.

where $\delta = \rho/\rho_c$ is the reduced density and $\tau = T_c/T$ is the inverse reduced temperature with ρ_c and T_c as the critical density and temperature, respectively; R is the specific gas constant. The numerical values of R, T_c , and ρ_c are given in Table I.

2.2.1. *The Helmholtz Energy for the Ideal Gas*

The ideal gas part of the dimensionless Helmholtz energy $A^o/(RT) = \Phi^o(\delta, \tau)$ has been correlated by the empirical equation

$$\Phi^o(\delta, \tau) = \ln(\delta) + a_1^o + a_2^o \tau + a_3^o \ln(\tau) + \sum_{i=1}^{I} b_i^o \tau^{t_i^o} \tag{2}$$

where $\delta = \rho/\rho_c$, and $\tau = T_c/T$. The values of the coefficients a_i^o, b_i^o and the exponents t_i^o are given in Table II. Equation (2) is valid in the temperature range $250 \leqslant T \leqslant 370$ K. The constants a_1^o and a_2^o were adjusted to give zero for the ideal gas enthalpy h^o at $T_o = 298.15$ K and for the ideal gas entropy s^o at $T_o = 298.15$ K and $p_o = 0.101325$ MPa. Thus, the zero points for enthalpy and entropy are

$$h^o(T_o = 298.15\ \text{K}) = 0$$

$$s^o(T_o = 298.15\ \text{K},\ p_o = 0.101325\ \text{MPa}) = 0$$

In Table III, all required derivatives of the ideal gas part Φ^o with respect to δ and τ are explicitly given. The numerical values of the coefficients a_3^o and b_i^o and the exponents t_i^o have been determined in the following way: For the one-atomic gas Ar, a_3^o is 1.5 and all b_i^o are zero. For the other two substances these values have been determined by fitting Eq. (2) to the isobaric specific heat capacities c_p^o in the ideal-gas state calculated from Setzmann's and Wagner's wide-range equation of state for CH_4 [3] and from the IUPAC equation of state for N_2 [7]. In the entire

Table II. Coefficients and Exponents of the Ideal-Gas Part Φ^{o}, Eq. (2), for CH_4, Ar, and N_2[a]

I	i	a_i^{o}	b_i^{o}	t_i^{o}
		Methane		
3	1	9.281098143	$0.1328142249 \times 10^{1}$	-1
	2	-6.774517024	$-0.2742139494 \times 10^{0}$	-2
	3	4.279504990	$0.1863016965 \times 10^{-1}$	-3
		Argon		
0	1	8.316662434		
	2	-4.946511643		
	3	1.500000000		
		Nitrogen		
1	1	10.26173163	$-0.1015833103 \times 10^{-6}$	-7
	2	-8.270504357		
	3	2.500571000		

[a] For the numerical values of T_c, ρ_c, and R, see Table I.

temperature range from 250 to 370 K, the differences between c_p^{o} values calculated from Eq. (2) and from the c_p^{o} equations given in Refs. 3 and 7 are less than $\pm 0.005\%$ for CH_4 and less than $\pm 0.003\%$ for N_2. Thus, the uncertainties of c_p^{o} values calculated from Eq. (2) for CH_4 and N_2 are estimated to be $\Delta c_p^{o}/c_p^{o} \leqslant \pm 0.02\%$ for CH_4 and $\Delta c_p^{o}/c_p^{o} \leqslant \pm 0.01\%$ for N_2.

Table III. The Ideal-Gas Part of the Dimensionless Helmholtz Energy Φ^{o} and Its Derivatives[a]

$$
\begin{array}{llllll}
\Phi^{o} = \ln(\delta) & + a_1^{o} & + a_2^{o}\tau & + a_3^{o}\ln(\tau) & + \sum_{i=1}^{I} b_i^{o}\tau^{t_i^{o}} \\
\Phi_{\delta}^{o} = 1/\delta & +0 & +0 & +0 & +0 \\
\Phi_{\delta\delta}^{o} = -1/\delta^2 & +0 & +0 & +0 & +0 \\
\Phi_{\delta\tau}^{o} = 0 & +0 & +0 & +0 & +0 \\
\Phi_{\tau}^{o} = 0 & +0 & + a_2^{o} & + a_3^{o}/\tau & + \sum_{i=1}^{I} b_i^{o} t_i^{o} \tau^{t_i^{o}-1} \\
\Phi_{\tau\tau}^{o} = 0 & +0 & +0 & - a_3^{o}/\tau^2 & + \sum_{i=1}^{I} b_i^{o} t_i^{o}(t_i^{o}-1)\tau^{t_i^{o}-2}
\end{array}
$$

[a] $\Phi_{\delta}^{o} = (\partial\Phi^{o}/\partial\delta)_{\tau}$, $\Phi_{\delta\delta}^{o} = (\partial^2\Phi^{o}/\partial\delta^2)_{\tau}$, $\Phi_{\tau}^{o} = (\partial\Phi^{o}/\partial\tau)_{\delta}$, $\Phi_{\tau\tau}^{o} = (\partial^2\Phi^{o}/\partial\tau^2)_{\delta}$, and $\Phi_{\delta\tau}^{o} = (\partial^2\Phi^{o}/\partial\delta\,\partial\tau)_{\tau\delta}$.

2.2.2. The Residual Part of the Helmholtz Energy

In order to determine the functional form for the residual part $\Phi^{\mathrm{r}}(\delta, \tau)$ of the Helmholtz energy we have developed a special strategy split into two steps.

The first step is the formulation of a general expression for the equation which functions as a "bank of terms." In order to keep the final equations for this special case of application as simple as possible, the bank of terms of the residual part of the dimensionless Helmholtz energy was formulated as a simple polynomial in δ and τ without including any exponential terms as is commonly used for wide-range equations of state. Thus, the bank of terms has the form

$$\Phi^{\mathrm{r}} = \sum_{i} \sum_{j} n_{ij} \delta^{d_i} \tau^{t_j} \tag{3}$$

where the exponents d_i range from 1 to 9 with a step width of 1 and the exponents t_j from -0.5 to 10 with a step width of 0.25. This means that the entire bank of terms contains 387 terms.

Table IV. Relations of Thermodynamic Properties to the Dimensionless Helmholtz Function Φ Consisting of Φ^{o} and Φ^{r} [See Eq. (1)]: The Form of the Equations for Φ^{o} and Φ^{r} is given by Eqs. (2) and (4), Respectively

Property	Relation[a]
Pressure	$\dfrac{p(\delta, \tau)}{\rho R T} = 1 + \delta \Phi^{\mathrm{r}}_{\delta}$
Internal energy	$\dfrac{u(\delta, \tau)}{R T} = \tau(\Phi^{\mathrm{o}}_{\tau} - \Phi^{\mathrm{r}}_{\tau})$
Enthalpy	$\dfrac{h(\delta, \tau)}{R T} = 1 + \tau(\Phi^{\mathrm{o}}_{\tau} + \Phi^{\mathrm{r}}_{\tau}) + \delta \Phi^{\mathrm{r}}_{\delta}$
Entropy	$\dfrac{s(\delta, \tau)}{R} = \tau(\Phi^{\mathrm{o}}_{\tau} + \Phi^{\mathrm{r}}_{\tau}) - \Phi^{\mathrm{o}} - \Phi^{\mathrm{r}}$
Isochoric specific heat capacity	$\dfrac{c_{\mathrm{v}}(\delta, \tau)}{R} = -\tau^2(\Phi^{\mathrm{o}}_{\tau\tau} + \Phi^{\mathrm{r}}_{\tau\tau})$
Isobaric specific heat capacity	$\dfrac{c_{\mathrm{p}}(\delta, \tau)}{R} = -\tau^2(\Phi^{\mathrm{o}}_{\tau\tau} + \Phi^{\mathrm{r}}_{\tau\tau}) + \dfrac{(1 + \delta \Phi^{\mathrm{r}}_{\delta} - \delta\tau \Phi^{\mathrm{r}}_{\delta\tau})^2}{1 + 2\delta \Phi^{\mathrm{r}}_{\delta} + \delta^2 \Phi^{\mathrm{r}}_{\delta\delta}}$
Speed of sound	$\dfrac{w^2(\delta, \tau)}{R T} = 1 + 2\delta \Phi^{\mathrm{r}}_{\delta} + \delta^2 \Phi^{\mathrm{r}}_{\delta\delta} - \dfrac{(1 + \delta \Phi^{\mathrm{r}}_{\delta} - \delta\tau \Phi^{\mathrm{r}}_{\delta\tau})^2}{\tau^2(\Phi^{\mathrm{o}}_{\tau\tau} + \Phi^{\mathrm{r}}_{\tau\tau})}$
Joule-Thomson coefficient	$\mu(\delta, \tau)\, R\rho = \dfrac{-(\delta \Phi^{\mathrm{r}}_{\delta} + \delta^2 \Phi^{\mathrm{r}}_{\delta\delta} + \delta\tau \Phi^{\mathrm{r}}_{\delta\tau})}{(1 + \delta \Phi^{\mathrm{r}}_{\delta} - \delta\tau \Phi^{\mathrm{r}}_{\delta\tau})^2 - \tau^2(\Phi^{\mathrm{o}}_{\tau\tau} + \Phi^{\mathrm{r}}_{\tau\tau})(1 + 2\delta \Phi^{\mathrm{r}}_{\delta} + \delta^2 \Phi^{\mathrm{r}}_{\delta\delta})}$

[a] $\Phi_{\delta} = (\partial\Phi/\partial\delta)_{\tau}$, $\Phi_{\delta\delta} = (\partial^2\Phi/\partial\delta^2)_{\tau}$, $\Phi_{\tau} = (\partial\Phi/\partial\tau)_{\delta}$, $\Phi_{\tau\tau} = (\partial^2\Phi/\partial\tau^2)_{\delta}$, and $\Phi_{\delta\tau} = (\partial^2\Phi/\partial\delta\,\partial\tau)_{\tau\delta}$.

Table V. The Residual Part Φ^r of the Dimensionless Helmholtz Energy and Its Derivatives

$$\Phi^r = \sum_{i=1}^{I} n_i \delta^{d_i} \tau^{t_i}$$

$$\Phi^r_\delta = \sum_{i=1}^{I} n_i d_i \delta^{d_i - 1} \tau^{t_i}, \qquad \Phi^r_{\delta\delta} = \sum_{i=1}^{I} n_i d_i (d_i - 1) \delta^{d_i - 2} \tau^{t_i}$$

$$\Phi^r_\tau = \sum_{i=1}^{I} n_i t_i \delta^{d_i} \tau^{t_i - 1}, \qquad \Phi^r_{\tau\tau} = \sum_{i=1}^{I} n_i \delta^{d_i} t_i (t_i - 1) \tau^{t_i - 2}$$

$$\Phi^r_{\delta\tau} = \sum_{i=1}^{I} n_i d_i t_i \delta^{d_i - 1} \tau^{t_i - 1}$$

In the second step, from the bank of terms, Eq. (3), the best combination of a limited number of terms has been determined by a special optimization procedure developed by Setzmann and Wagner [8]. In this fitting and optimization process, only input data of

- thermal properties $p(T, \rho)$ and
- speeds of sound $w(T, p)$

were used, since experimental c_p and c_v data were not available in a sufficient number and accuracy. In order to take into account the so-called "nonlinear" data $w(T, p)$ when optimizing the structure of the final Φ^r equation, the linear optimization procedure [8] has been combined in an iterative way with a nonlinear fitting to all data, linear and nonlinear. This entire fitting and optimization process is described in detail by Setzmann and Wagner [3]. Details with regard to single data sets used for CH_4, Ar, and N_2 are given in Sections 3.1 to 3.3.

Table VI. Thermodynamic Property Values for $T = 323.15$ K at $p = 10$ MPa Calculated from Eq. (5) for the Density and from Eqs. (2) and (4) for the Caloric Properties

Property	CH_4	Ar	N_2
ρ (kg · m^{-3})	66.59483	152.74432	102.49547
c_v (kJ · kg^{-1} · K^{-1})	1.84418	0.32530	0.75904
c_p (kJ · kg^{-1} · K^{-1})	2.86515	0.62238	1.16480
w (m · s^{-1})	465.52546	351.97120	393.97879
h (kJ · kg^{-1})	−28.06957	−2.46921	9.62673
s (kJ · kg^{-1} · K^{-1})	−2.39902	−0.95468	−1.33216
u (kJ · kg^{-1})	−178.23137	−67.93810	−87.93856
μ (K · MPa^{-1})	2.81926	2.28940	1.16049

Table VII. Summary of the Literature on Preselected Experimental p-ρ-T Data for Methane in the Fitting Range of the Equation ($270 \leqslant T \leqslant 350$ K, $p \leqslant 30$ MPa)

		Number of data			Uncertainty[a]		
Source	Year	Total	Fitting range	Selected	ΔT (mK)	$\Delta p/p$ (%)	$\Delta \rho/\rho$ (%)
Schamp et al. [9]	1958	118	68	0	±10	±0.003	(±0.05)
Douslin et al. [10]	1964	374	119	0	±1	±0.03	±0.03 to ±0.2
Roe [11]	1972	82	6	6	±5	±0.08	(±0.02 to ±0.05)
Goodwin & Prydz [12, 13]	1972	554	47	47	—	—	(±0.05 to ±0.3)
Trappeniers et al. [14]	1979	472	226	226[b]	±3	±0.01	(±0.05)
Mollerup [15]	1985	51	46	0	±30	—	±0.1
Achtermann et al. [16]	1986	35	35	35[b]	—	—	(±0.05)
Kleinrahm et al. [17]	1988	169	169	169	±3	±0.007	±0.02
Pieperbeck et al. [18]	1991	175	157	157	±5	±0.007	±0.02
Jaeschke & Hinze [19]	1991	716	716	301[b]	—	—	±0.05
Achtermann et al. [20]	1992	654	505	198[b]	—	—	±0.05

[a] Uncertainty values given in parentheses were estimated by ourselves.

[b] For $p \leqslant 12$ MPa, data with $\Delta \rho/\rho > \pm 0.02\,\%$ were used with reduced weighting factors.

Table VIII. Summary of the Literature on Preselected Experimental Caloric Data for Methane in the Fitting Range of the Equation ($270 \leqslant T \leqslant 350$ K, $p \leqslant 30$ MPa)

		Number of data			
Source	Year	Total	Fitting range	Selected	Uncertainty[a]
		Speed of sound w			$\Delta w/w$ (%)
Straty [21]	1974	61	6	6	±0.05 to ±0.2
Gammon & Douslin [22]	1976	197	8	8	±0.01 to ±1
Sivaraman & Gammon [23]	1986	95	34	34	(±0.01 to ±1)
Goodwin [24]	1988	108	80	80	(±0.02)
Lemming [25]	1989	62	28	28	±0.01
Trusler & Zarari [26]	1992	80	64	64	±0.002
		Isochoric specific heat capacity c_v			$\Delta c_v/c_v$ (%)
Younglove [27]	1974	283	14	0	(±1 to ±5)
		Isobaric specific heat capacity c_p			$\Delta c_p/c_p$ (%)
Budenholzer et al. [28]	1939	42	20	0	(±2)
Jones et al. [29]	1963	400	36	0	(±2)

[a] Uncertainty values given in parentheses were estimated by ourselves.

Table IX. Coefficients and Exponents of Eqs. (4) and (5) for CH_4

i	d_i	t_i	n_i
1	1	−0.25	$0.251330485 \times 10^{0}$
2	1	1.50	$-0.139629073 \times 10^{1}$
3	1	6.25	$-0.161847554 \times 10^{-1}$
4	2	0.25	$0.837623969 \times 10^{-1}$
5	2	3.00	$0.204359144 \times 10^{0}$
6	2	5.50	$-0.100523656 \times 10^{0}$
7	3	−0.25	$0.167341616 \times 10^{-1}$
8	3	2.25	$-0.598535889 \times 10^{-1}$
9	3	5.00	$0.115937043 \times 10^{0}$
10	4	4.00	$-0.496627097 \times 10^{-1}$
11	5	1.25	$0.957140954 \times 10^{-2}$
$12 = I$	8	4.25	$0.113228746 \times 10^{-3}$

In this way, for each of the three substances a residual part of the Helmholtz function $\Phi^{\mathrm{r}} = A^{\mathrm{r}}(\delta, \tau)/(RT)$ of the general form

$$\Phi^{\mathrm{r}} = \sum_{i=1}^{I} n_i \delta^{d_i} \tau^{t_i} \tag{4}$$

has been determined, where $\delta = \rho/\rho_{\mathrm{c}}$ and $\tau = T_{\mathrm{c}}/T$. Together with the coefficients n_i and the exponents d_i and t_i, given for CH_4, Ar, and N_2 in Sections 3.1 to 3.3, respectively, Eq. (4) forms an equation of state which is valid in the region

$$270 \leqslant T \leqslant 350\ \mathrm{K}$$
$$0 < p \leqslant 30\ \mathrm{MPa}$$

As a result of tests, we found that the equations for argon and methane can also be used in a slightly enlarged temperature range from 250 to 370 K at pressures up to 30 MPa without an essential loss of accuracy. Due to limitations of the data set (cf. Section 3.3) the equation for nitrogen was not tested in an enlarged temperature range.

Table IV lists the relations between the dimensionless Helmholtz function Φ consisting of Φ°, Eq. (2), and Φ^{r}, Eq. (4), and the most important thermodynamic properties, which might be of interest for the applications considered in this paper. To simplify the application of Eq. (4) for calculating the desired property, the necessary derivatives of Φ^{r} with respect to δ and τ are explicitly given in Table V. Thus, with the help of Tables III–V, the most important thermodynamic properties of CH_4, Ar, and N_2 can be calculated from Eqs. (2) and (4) in a fairly simple way.

Fortunately, the most important relation for the application

Table X. Estimated Uncertainties in ρ, w, c_{p}, and c_{v} of the New Equation of State for CH_4 for Temperatures from 270 to 350 K

Property	Pressure range (MPa)	Uncertainty (%)[a]
p-ρ-T	$0 < p \leqslant 12$	$\Delta\rho/\rho \leqslant \pm 0.02$
	$12 < p \leqslant 30$	$\Delta\rho/\rho \leqslant \pm 0.05$
w	$0 < p \leqslant 10$	$\Delta w/w \leqslant \pm 0.02$
	$10 < p \leqslant 30$	$\Delta w/w \leqslant \pm 0.1$
c_{p}	$0 < p \leqslant 30$	$\Delta c_{\mathrm{p}}/c_{\mathrm{p}} \leqslant \pm 1$
c_{v}	$0 < p \leqslant 30$	$\Delta c_{\mathrm{v}}/c_{\mathrm{v}} \leqslant \pm 1$

[a] The values correspond to a probability level of 95%.

considered here, namely, the thermal equation of state, can be directly used to calculate the density by iteration:

$$\frac{p}{RT\rho} = z = 1 + \sum_{i=1}^{I} n_i d_i \delta^{d_i} \tau^{t_i} \qquad (5)$$

with $\delta = \rho/\rho_c$ and $\tau = T_c/T$. The values of the coefficients n_i and the exponents d_i and t_i are given in Sections 3.1 to 3.3.

To assist the user in computer-program verification, Table VI lists values for some selected properties of CH_4, Ar, and N_2 calculated from Eq. (5) for the density and from Eqs. (2) and (4) for some caloric properties at $T = 323.15$ K and $p = 10$ MPa.

3. THE NEW EQUATIONS OF STATE FOR METHANE, ARGON, AND NITROGEN

In this section the numerical values of the coefficients and exponents of the new equations of state for CH_4, Ar, and N_2 are given. These values define, together with Eqs. (2) and (4) or (5), respectively, the new equations of state for the three substances. In addition to this, information about the experimental data used to develop the equations, the estimated uncertainties of the equations and comparisons with experimental data are presented.

3.1. The Equation of State for Methane

Based on the data selection carried out in the paper of Setzmann and Wagner [3] on the wide-range equation of state for CH_4, Table VII gives a summary of the literature on preselected experimental p-ρ-T data of methane which are, at least partly, in the temperature and pressure range considered here. The number of data points which are in the fitting range and how many of them were finally selected to develop the new equation can be seen. Moreover, the uncertainty of the data estimated by the authors or by ourselves is listed. Table VIII summarizes the corresponding information on the experimental data of the caloric properties w, c_p, and c_v. Table VII shows that the new equation for methane was developed by the use of eight p-ρ-T data sets. However, in the pressure range $p \leqslant 12$ MPa the equation is based mainly on the data of Kleinrahm et al. [17] and Pieperbeck et al. [18], which already have the required uncertainty in density of $\Delta\rho/\rho \leqslant \pm 0.02\,\%$. In this pressure range, the data sets of the other authors listed under the column "Selected" were used with a reduced weighting factor. However, for pressures $p > 12$ MPa these data were used with the "normal" weighting factor corresponding to their estimated uncertainty. From the caloric properties, only six data sets of the speed of sound were used; see Table VIII. The c_p and c_v data are not accurate enough and cover too small a region to be used to develop the CH_4 equation.

Tables II and IX list the coefficients and exponents which define, together with Eqs. (2) and (4) or (5), respectively, the new equation of

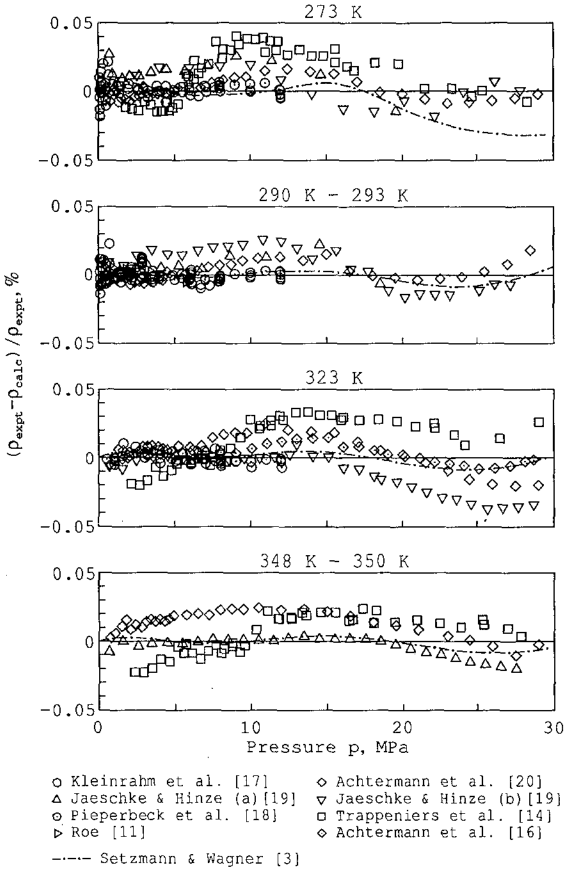

Fig. 1. Percentage density deviations of selected p-ρ-T data from values calculated with the new equation of state for methane. The dash-dot line corresponds to values calculated from the wide-range equation of state of Setzmann and Wagner [3]. Jaeschke and Hinze [19] published results of Burnett measurements (a) and of refractive index measurements (b).

state for methane; the needed values for R, T_c, and ρ_c can be taken from Table I. All the desired caloric properties of CH_4 can be calculated from Eq. (1), consisting of Eqs. (2) and (4), and the thermal properties from Eq. (4) or directly from Eq. (5).

Table X contains the estimated uncertainties of the new 12-term equation of state for CH_4 with regard to ρ, w, c_p, and c_v in the corresponding pressure ranges for temperatures from 270 to 350 K. It can be seen that the uncertainty of the new equation in density is $\leqslant \pm 0.02\%$ for $p \leqslant 12$ MPa and $\leqslant \pm 0.05\%$ for higher pressures. Based on the good speed-of-sound

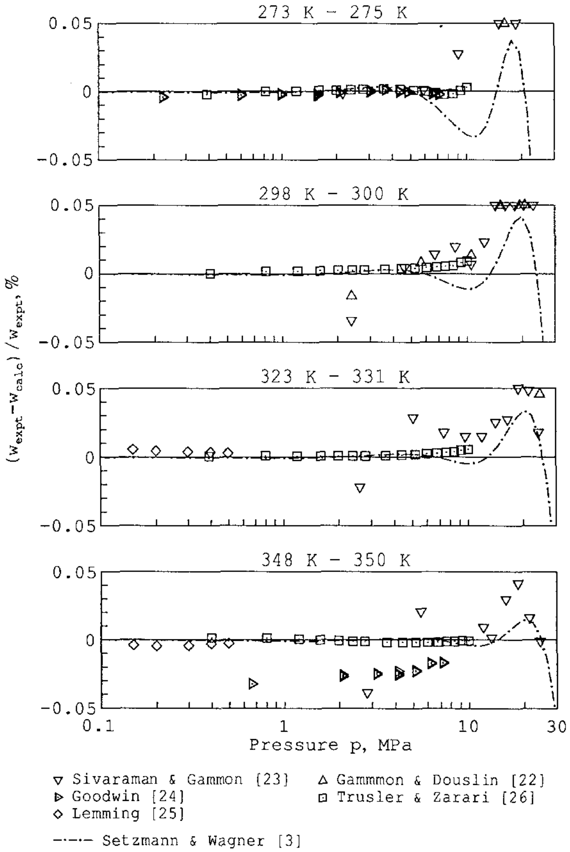

Fig. 2. Percentage deviations of selected experimental speeds of sound w from values calculated with the new equation of state for methane. The dash-dot line corresponds to values calculated from the wide-range equation of state of Setzmann and Wagner [3].

Table XI. Summary of the Literature on Preselected Experimental p-ρ-T Data for Argon in the Fitting Range of the Equation ($270 \leqslant T \leqslant 350$ K, $p \leqslant 30$ MPa)

		Number of data			Uncertainty[a]		
Source	Year	Total	Fitting range	Selected	ΔT (mK)	$\Delta p/p$ (%)	$\Delta\rho/\rho$ (%)
Baxter & Starkweather [30]	1928	3	3	0	—	—	(±0.05)
Michels et al. [31]	1949	355	113	105[b]	—	—	(±0.03)
Townsend [32]	1956	36	36	0	±10	—	(±0.1)
Crain & Sonntag [33]	1966	78	22	0	±10	±0.016	±0.1
Blancett et al. [34]	1970	74	42	0	—	—	±0.06
Rabinovich et al. [35]	1970	61	16	0	±50	±0.032	±0.08
Cheng [36]	1972	268	1	0	±15	±0.2 MPa	±0.1
Hoinkis [37]	1989	46	38	0	—	—	±0.56
Guo et al. [38]	1992	28	28	28	±5	±0.007	±0.02
Gilgen et al. [4]	1993	638	91	91	±1.5	±0.006	±0.015

[a] Uncertainty values given in parentheses were estimated by ourselves.

[b] For $p \leqslant 12$ MPa, data with $\Delta\rho/\rho > \pm 0.02\,\%$ were used with reduced weighting factors.

data the uncertainty in w ranges from $\leqslant \pm 0.02\%$ for $p \leqslant 10$ MPa to $\leqslant \pm 0.1\%$ for higher pressures. The higher uncertainties in c_p and c_v of $\leqslant \pm 1\%$ are due to the lack of accurate experimental data of these properties.

For four representative isotherms, Fig. 1 shows the percentage density deviations of experimental p-ρ-T data from density values calculated from Eq. (5) for CH_4. The p-ρ-T data which deviate for $p \leqslant 12$ MPa by more than $\pm 0.02\%$ in density have uncertainties greater than those of the primary data ($\Delta\rho/\rho \leqslant \pm 0.02\%$) on which the equation is mainly based in this region. In the entire region, the equation clearly represents all the preselected p-ρ-T data within the experimental uncertainty estimated for these data sets, see Table VII. Figure 2 shows the corresponding deviation diagrams with regard to the speed of sound.

Table XII. Summary of the Literature on Preselected Experimental Caloric Data for Argon in the Fitting Range of the Equation ($270 \leqslant T \leqslant 350$ K, $p \leqslant 30$ MPa)

Source	Year	Number of data			Uncertainty[a]
		Total	Fitting range	Selected	
		Speed of sound w			$\Delta w/w$ (%)
Lacam & Noury [39]	1953	60	16	0	±1 (to ±2)
Lacam & Noury [40]	1953	12	12	0	±1 (to ±2)
Lacam [41]	1956	152	15	5	(±1 to ±1.5)
van Itterbeek et al. [42]	1959	79	25	11	(±0.2 to ±0.6)
Lestz [43]	1963	14	14	0	(±0.2)
Susekov [44]	1972	11	11	11	(±0.5)
Goodwin [24]	1988	56	44	43	(±0.02)
		Isochoric specific heat capacity c_v			$\Delta c_v/c_v$ (%)
Michels et al. [45][b]	1949	126	32	0	(±0.5)
Lestz [43][c]	1963	14	14	0	(±0.5)
		Isobaric specific heat capacity c_p			$\Delta c_p/c_p$ (%)
Michels et al. [45][b]	1949	126	32	0	(±0.5)
Lestz [43][c]	1963	14	14	0	(±0.5)

[a] Uncertainty values given in parentheses were estimated by ourselves.

[b] Calculated by Michels et al. [45] from their p-ρ-T measurements [31].

[c] Calculated by Lestz from his speed of sound measurements [43].

Table XIII. Coefficients and Exponents of Eqs. (4) and (5) for Ar

i	d_i	t_i	n_i
1	1	0.25	$0.902906714 \times 10^{0}$
2	1	1.00	$-0.189621232 \times 10^{1}$
3	1	4.00	$-0.179790530 \times 10^{0}$
4	2	0.25	$0.854553290 \times 10^{-1}$
5	2	2.75	$0.152713256 \times 10^{0}$
6	3	-0.50	$0.994079499 \times 10^{-2}$
7	3	2.50	$-0.359988775 \times 10^{-1}$
$8 = I$	5	0.25	$0.332254806 \times 10^{-2}$

3.2. The Equation of State for Argon

Table XI gives a summary of the literature on preselected experimental p-ρ-T data for argon which are, at least partly, in the temperature and pressure range considered here. The number of data points which are in the fitting range and how many of them were finally selected to develop the new equation can be seen. Moreover, the uncertainty of the data estimated by the authors or by ourselves is listed. Table XII summarizes the corresponding information on the experimental data of the caloric properties w, c_p, and c_v. Table XI shows that the new equation for argon was developed by the use of the very accurate p-ρ-T data of Michels et al. [31][4] and of

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[4] The only data of Michels et al. which were excluded are the measuring run on the 273 K isotherm obtained with "volume C" (see Ref. 31), since it resulted in data which deviate systematically from the other runs.

Table XIV. Estimated Uncertainties in ρ, w, c_p, and c_v of the New Equation of State for Ar for Temperatures from 270 to 350 K

Property	Pressure range (MPa)	Uncertainty (%)[a]
p-ρ-T	$0 < p \leqslant 12$	$\Delta\rho/\rho \leqslant \pm 0.02$
	$12 < p \leqslant 30$	$\Delta\rho/\rho \leqslant \pm 0.05$
w	$0 < p \leqslant 7$	$\Delta w/w \leqslant \pm 0.1$
	$7 < p \leqslant 30$	$\Delta w/w \leqslant \pm 0.3$
c_p	$0 < p \leqslant 30$	$\Delta c_p/c_p \leqslant \pm 1$
c_v	$0 < p \leqslant 30$	$\Delta c_v/c_v \leqslant \pm 1$

[a] The values correspond to a probability level of 95%.

the two data sets measured in our group, namely, by Guo et al. [38] and by Gilgen et al. [4]. Fortunately, the data of these authors cover the range, in which the equation has been fitted, sufficiently well. All the other data are not accurate enough to be used to develop the equation of state. With regard to the caloric properties, only the speed-of-sound data measured by Lacam [41], by van Itterbeek et al. [42], by Susekov [44], and by Goodwin [24] were used to develop the equation. All the other data are not accurate enough or are not direct experimental data.

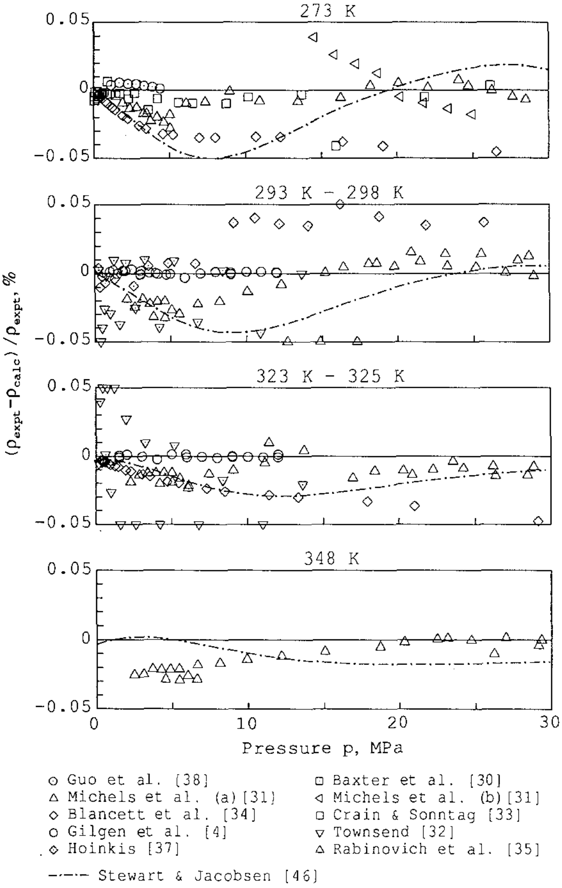

Fig. 3. Percentage deviations of preselected p-ρ-T data from values calculated with the new equation of state for argon. The dash-dot line corresponds to values calculated from the wide-range equation of state of Stewart and Jacobsen [46]. The data of Michels et al. [31] indicated by (b) were excluded from the fitting procedure.

Tables II and XIII list the coefficients and exponents which define, together with Eqs. (2) and (4) or (5), respectively, the new equation of state for argon; the needed values for R, T_c, and ρ_c can be taken from Table I. All the desired caloric properties of Ar can be calculated from Eq. (1), consisting of Eqs. (2) and (4), and the thermal properties from Eq. (4) or directly from Eq. (5).

Table XIV contains the estimated uncertainties of the new eight-term equation of state for Ar with regard to ρ, w, c_p, and c_v in the corresponding pressure ranges for temperatures from 270 to 350 K. It can be seen that the uncertainty of the new equation in density is $\leqslant \pm 0.02\%$ for $p \leqslant 12$ MPa and $\leqslant \pm 0.05\%$ for higher pressures. The higher uncertainties in the caloric properties are due to the uncertainty of the experimental data in w, c_p, and c_v. For $T \leqslant 300$ K and $p \leqslant 7$ MPa, Eq. (1) reproduces Goodwin's speed-of-sound data [24] clearly within $\Delta w/w \leqslant \pm 0.05\%$. Since, however, for higher temperatures there are no speed-of-sound data of similar accuracy, we have estimated the uncertainty of Eq. (1) with regard to speed of sound to be $\Delta w/w \leqslant \pm 0.1\%$ for $p \leqslant 7$ MPa in the entire temperature range.

For four representative isotherms, Fig. 3 shows percentage density deviations of experimental p-ρ-T data from density values calculated from Eq. (5) for Ar. The p-ρ-T data on which the equation of state is based [31,

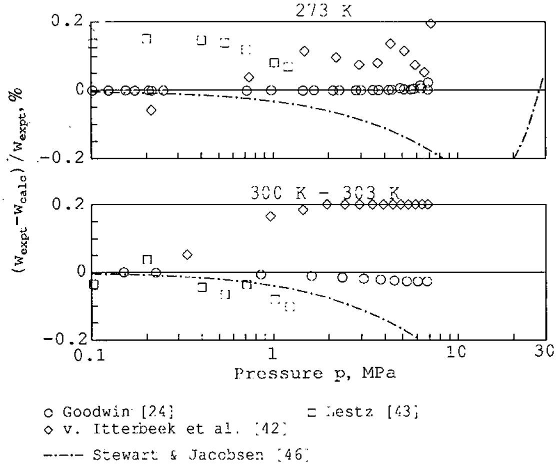

Fig. 4. Percentage deviations of preselected experimental speeds of sound w from values calculated with the new equation of state for argon. The dash-dot line corresponds to values calculated from the wide-range equation of state of Stewart and Jacobsen [46].

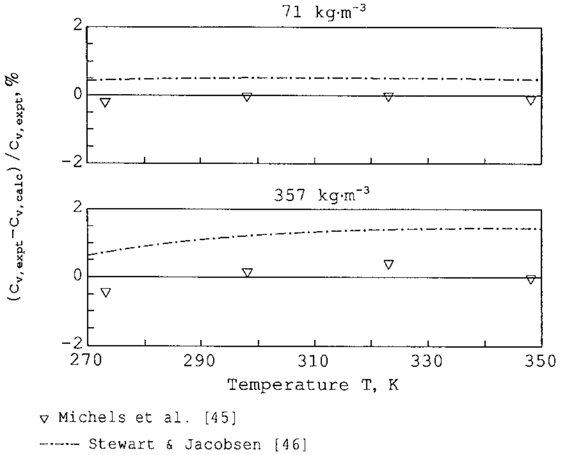

Fig. 5. Percentage deviations of preselected isochoric specific heat capacities c_v from values calculated with the new equation of state for argon. The dash-dot line corresponds to values calculated from the wide-range equation of state of Stewart and Jacobsen [46].

38, 4] are represented within their experimental uncertainty. The plot of density values calculated from the wide-range equation of state developed by Stewart and Jacobsen [46] is given for comparison.

Figures 4 and 5 show deviation diagrams of the speed of sound and the isochoric specific heat capacity on two representative isotherms and isochores, respectively. The experimental data are clearly represented within the estimated uncertainties of the equation of state.

3.3. The Equation of State for Nitrogen

Based on the report of Watson and de Reuck [47], Table XV gives a summary of the literature on preselected p-ρ-T data for nitrogen in the temperature and pressure range considered here. The number of data points which are in the fitting range and how many of them were finally selected to develop the new equation can be seen. Moreover, the uncertainty of the data estimated by the authors or by ourselves is listed. Table XVI summarizes the corresponding information on the experimental data of the caloric properties w, c_p, and c_v. Table XV shows that the new equation for nitrogen was developed by the use of eight p-ρ-T data sets. However, in the pressure range $p \leqslant 12$ MPa the equation is based mainly on the data sets of Duschek et al. [52] and Pieperbeck et al. [18], which already have the required uncertainty in density of $\Delta\rho/\rho \leqslant \pm 0.02\%$. In this

Table XV. Summary of the Literature on Preselected Experimental p-ρ-T Data for Nitrogen in the Fitting Range of the Equation ($270 \leqslant T \leqslant 350$ K, $p \leqslant 30$ MPa)

Source	Year	Number of data			Uncertainty[a]		
		Total	Fitting range	Selected	ΔT (mK)	$\Delta p/p$ (%)	$\Delta\rho/\rho$ (%)
Michels et al. [48]	1934	56	32	0	—	—	(±0.05)
Otto et al. [49]	1934	63	36	36[b]	—	—	(±0.05)
Michels et al. [50]	1936	147	14	14[b]	—	—	(±0.05)
Crain & Sonntag [33]	1966	90	21	21[b]	±10	±0.016	±0.1
Roe [11]	1972	80	12	0	±5	±0.08	to ±0.05
Boden [51]	1984	7	7	0	—	—	(±0.05)
Achtermann et al. [16]	1986	35	35	35[b]	—	±0.005	(±0.05)
Duschek et al. [52]	1988	127	127	127	±3	±0.007	±0.02
Jaeschke & Hinze [19][c]	1991	129	129	129[b]	—	—	(±0.05)
Jaeschke & Hinze [19][d]	1991	514	514	514[b]	—	—	(±0.05)
Pieperbeck et al. [18]	1991	124	124	124	±5	±0.007	±0.02

[a] Uncertainty values given in parentheses were estimated by ourselves.

[b] For $p \leqslant 12$ MPa, data with $\Delta\rho/\rho > \pm 0.02\%$ were used with reduced weighting factors.

[c] Burnett method.

[d] From measurements of the refractive index.

Table XVI. Summary of the Literature on Preselected Experimental Caloric Data for Nitrogen in the Fitting Range of the Equation ($270 \leqslant T \leqslant 350$ K, $p \leqslant 30$ MPa)

Source	Year	Number of data			Uncertainty[a]
		Total	Fitting range	Selected	
		Speed of sound w			$\Delta w/w$ (%)
Lestz [43]	1963	15	15	0	(to ±0.2)
Voronov et al. [53]	1969	113	2	0	±0.3
Susekov [44]	1972	10	10	0	(±0.5)
Younglove & McCarty [54]	1980	237	51	51	±0.03
		Isochoric specific heat capacity c_v			$\Delta c_v/c_v$ (%)
Lestz [43][b]	1963	15	15	0	(±0.5)
		Isobaric specific heat capacity c_p			$\Delta c_p/c_p$ (%)
Workman [55]	1931	14	14	0	(±0.5)
Lestz [43][b]	1963	15	15	0	(±0.5)

[a] Uncertainty values given in parentheses were estimated by ourselves.
[b] Calculated by Lestz from his speed of sound measurements [43].

pressure range, the data sets of the other authors were used with a reduced weighting factor. However, for pressures $p > 12$ MPa these data were used with the "normal" weighting factor corresponding to their estimated uncertainty. With regard to caloric properties, only the speed-of-sound data of Younglove and McCarty were used to develop Eq. (4); cf. Table XVI. All the other data are not accurate enough or are not direct measurements.

Tables II and XVII list the coefficients and exponents which define,

Table XVII. Coefficients and Exponents of Eqs. (4) and (5) for N_2

i	d_i	t_i	n_i
1	1	0.00	$0.465818264 \times 10^{0}$
2	1	1.25	$-0.152191402 \times 10^{1}$
3	1	4.00	$-0.395485009 \times 10^{-1}$
4	2	0.75	$0.169916530 \times 10^{0}$
5	3	0.00	$0.785673046 \times 10^{-1}$
6	3	0.50	$-0.118412137 \times 10^{0}$
$7 = I$	4	1.00	$0.219346719 \times 10^{-1}$

Table XVIII. Estimated Uncertainties in ρ, w, c_p, and c_v of the New Equation of State for N_2 for Temperatures from 270 to 350 K

Property	Pressure range (MPa)	Uncertainty (%)[a]
p-ρ-T	$0 < p \leqslant 12$	$\Delta\rho/\rho \leqslant \pm 0.02$
	$12 < p \leqslant 30$	$\Delta\rho/\rho \leqslant \pm 0.05$
w	$0 < p \leqslant 1.5$	$\Delta w/w \leqslant \pm 0.1$
	$1.5 < p \leqslant 30$	$\Delta w/w \leqslant \pm 0.5$
c_p	$0 < p \leqslant 30$	$\Delta c_p/c_p \leqslant \pm 1$
c_v	$0 < p \leqslant 30$	$\Delta c_v/c_v \leqslant \pm 1$

[a] The values correspond to a probability level of 95%.

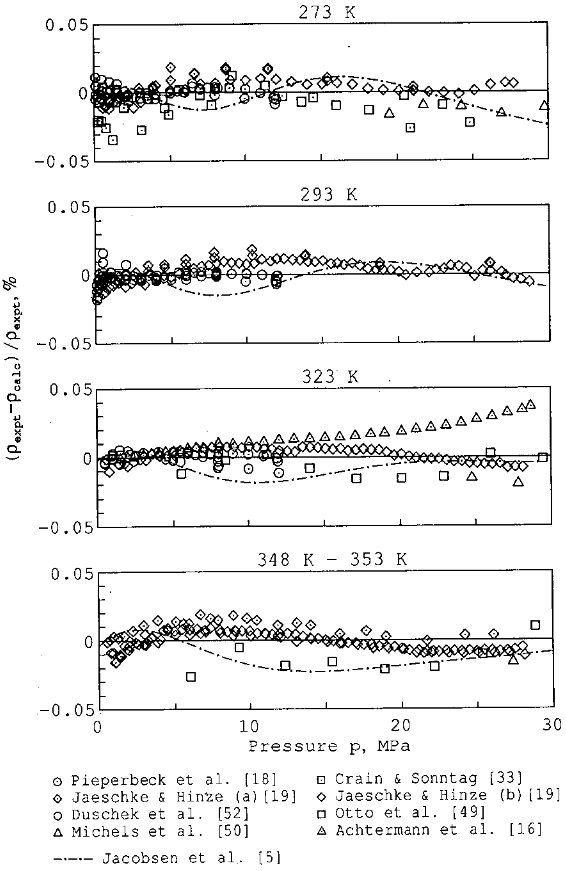

Fig. 6. Percentage density deviations of selected p-ρ-T data from values calculated with the new equation of state for nitrogen. The dash-dot line corresponds to values calculated from the wide-range equation of state of Jacobsen et al. [5]. Jaeschke and Hinze [19] published results of Burnett measurements (a) and of refractive index measurements (b).

together with Eqs. (2) and (4) or (5), respectively, the new equation of state for nitrogen; the needed values for R, T_c, and ρ_c can be taken from Table I. All the desired caloric properties of N_2 can be calculated from Eq. (1), consisting of Eqs. (2) and (4), and the thermal properties from Eq. (4) or directly from Eq. (5).

Table XVIII contains the estimated uncertainties of the new seven-term equation of state for N_2 with regard to ρ, w, c_p, and c_v in the corresponding pressure ranges for temperatures from 270 to 350 K. It can be seen that the uncertainty of the new equation in density is $\leqslant \pm 0.02\%$ for $p \leqslant 12$ MPa and $\leqslant \pm 0.05\%$ for higher pressures. The uncertainty in speed of sound is $\leqslant \pm 0.1\%$ for $p \leqslant 1.5$ MPa and $\leqslant \pm 0.5\%$ for higher pressures. The higher uncertainties in c_p and c_v of $\leqslant \pm 1\%$ are due to the accuracy of the very few experimental data.

For four representative isotherms, Fig. 6 shows percentage density deviations of experimental p-ρ-T data from density values calculated from Eq. (5) for N_2. The p-ρ-T data which deviate for $p \leqslant 12$ MPa by more than $\pm 0.02\%$ in density have uncertainties greater than those of the primary data ($\Delta\rho/\rho \leqslant \pm 0.02\%$) on which the new equation of state is mainly based in this region. For $p > 12$ MPa, the data are also clearly represented within their uncertainty. The plot of density values calculated from the wide-range equation of state developed by Jacobsen et al. [5] is given for comparison.

Figures 7 and 8 show deviation diagrams of the speed of sound and

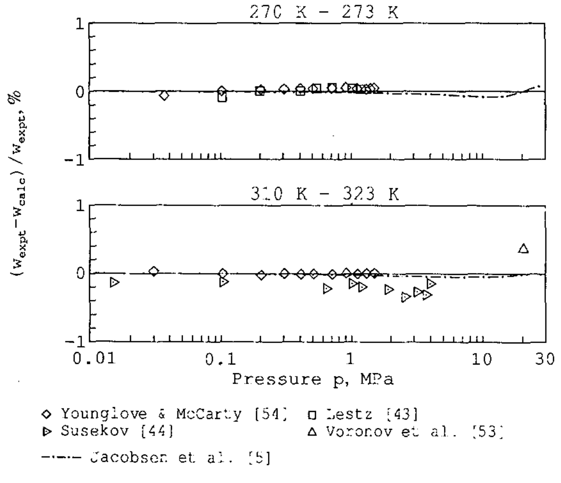

Fig. 7. Percentage deviations of preselected speeds of sound w from values calculated with the new equation of state for nitrogen. The dash-dot line corresponds to values calculated from the wide-range equation of state of Jacobsen et al. [5].

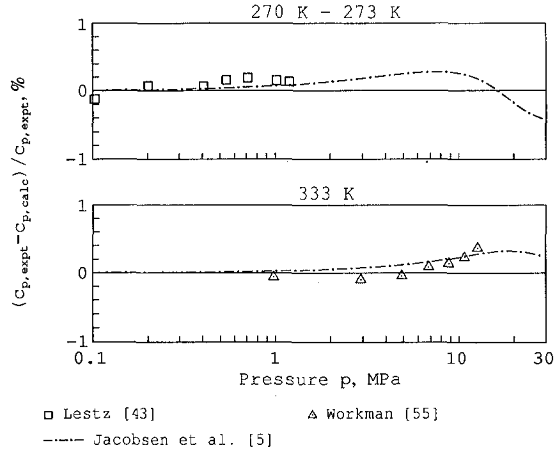

Fig. 8. Percentage deviations of preselected isobaric specific heat capacities c_p from values calculated with the new equation of state for nitrogen. The dash-dot line corresponds to values calculated from the wide-range equation of state of Jacobsen et al. [5].

the isobaric specific heat capacity on two representative isotherms. The experimental data, which were not used for the development of the equation, are clearly represented within the estimated uncertainties of the equation of state for these properties.

4. CONCLUSION

Within the framework of the EUROMET project "Gas Density," short equations of state for the gas and supercritical region of the three pure substances methane, argon, and nitrogen have been developed. These equations are in form of the Helmholtz energy, consisting of an ideal-gas part and a residual part taking into account the real fluid behavior. The functional form of the residual parts has been obtained with a special optimization procedure [8] to optimize the structure of these equations. The new equations of state for CH_4, Ar, and N_2 having 12, 8, and 7 fitted coefficients, respectively, cover the "natural-gas region," namely, the temperature range from 270 to 350 K at pressures up to 30 MPa.

For the pressure range $p \leqslant 12$ MPa, the new equations of state for all three substances already meet the uncertainty requirement in density of $\Delta\rho/\rho \leqslant \pm 0.02\,\%$. With regard to the density calculation for $p > 12$ MPa (at present the uncertainty is $\Delta\rho/\rho \leqslant \pm 0.05\,\%$) and to the calculation of the caloric properties in the entire region (with the exception of the speed of sound for methane in the entire pressure range, for argon at $p \leqslant 7$ MPa, and for nitrogen at $p \leqslant 1.5$ MPa), the equations do not meet the high requirements for the applications considered here but they are as accurate as possible based on the present situation of the experimental data.

In order to develop equations of state which are able to meet all the accuracy requirements (see Section 2.1), more accurate density measurements for $p > 12$ MPa and much more accurate measurements of caloric data (especially speeds of sound at higher pressures and isobaric specific heat capacities) are absolutely necessary. As soon as these data are available, the equations should be correspondingly revised.

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NOMENCLATURE

A	Specific Helmholtz energy
a, b, n	Adjustable coefficients
c_p	Isobaric specific heat capacity
c_v	Isochoric specific heat capacity
d, t	Exponents
h	Specific enthalpy
I	Maximum value of the serial number i
i, j	Serial numbers
p	Pressure
R	Specific gas constant
R_m	Molar (universal) gas constant
s	Specific entropy
T	Absolute temperature
u	Internal energy
w	Speed of sound
$z = p/(\rho RT)$	Compression factor
Δ	Difference in a quantity
$\delta = \rho/\rho_c$	Reduced density
∂	Partial differential
μ	Joule–Thomson coefficient
ρ	Mass density
$\tau = T_c/T$	Inverse reduced temperature
$\Phi = A/(RT)$	Dimensionless Helmholtz energy

Superscripts

o	Ideal-gas property
r	Residual

Subscripts

c	At the critical point
expt	Experimental
calc	Calculated
i, *j*	Serial numbers
o	Reference state

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