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Thermodynamic Properties of Methane in the Critical Region

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A scaled fundamental equation is presented for the thermodynamic properties of methane in the critical region. The equation supplements the international formulation for the thermodynamic properties of methane issued by IUPAC.

KEY WORDS: critical parameters; critical phenomena; equation of state; methane; sound velocity; specific heat; thermodynamic properties.

1. INTRODUCTION

Methane is one of the most important hydrocarbons and accurate information on its thermodynamic properties is desired for many applications. Several attempts have been made to formulate representative equations for the thermodynamic properties of methane over a large range of temperatures and pressures [1, 2] culminating in an international formulation issued by IUPAC [3]. The IUPAC formulation is an analytic equation that fails to account for the expected singular behavior of the thermodynamic properties near the critical point. The global equation of Goodwin includes a partial attempt to address this problem [2].

Theory predicts that the behavior of the thermodynamic properties close to the critical point satisfies scaling laws with universal critical exponents and universal scaling laws [4]. Scaled equations of state for methane in the critical region have been proposed by Gielen et al. [5], by Chapela and Rowlinson [6], and by Anisimov et al. [7]. These previous scaled equations of state contain effective critical-exponent values that dif-

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fer from the universal exponent values predicted theoretically [4]. Furthermore, as is evident from the paper by Anisimov et al. [7], previous investigators did not have sufficient experimental information for methane in the critical region. As discussed in earlier publications, it is possible to represent the thermodynamic properties of fluids near the critical point in terms of a revised and extended scaled fundamental equation with universal critical-exponent values [4, 8]. The lack of adequate experimental information has also been remedied. New experimental pressure and density measurements have been reported by Kleinrahm et al. [9, 10], and new sound-velocity data by Sivaraman and Gammon [11], supplementing the earlier sound-velocity data of Gammon and Douslin [12]. As a consequence, it has become possible to formulate a scaled fundamental equation for the thermodynamic properties of methane in the critical region.

2. SCALED FUNDAMENTAL EQUATION

The scaled fundamental equation adopted in this paper was originally proposed by Balfour et al. [13] and has been used previously to represent the thermodynamic properties of light steam [14], heavy steam [15], isobutane [16], ethylene [17], and carbon dioxide [18] in the critical region. The fundamental equation is expressed in terms of the intensive variables, namely, the pressure P, the temperature T, and the chemical potential μ. Specifically, we consider the potential P/T as a function of $-1/T$ and μ/T. The thermodynamic variables are made dimensionless with the aid of the critical pressure P_c, the critical temperature T_c, and the critical density ρ_c:

$$\tilde{P}=\frac{P}{T}\frac{T_c}{P_c}, \qquad \tilde{T}=-\frac{T_c}{T}, \qquad \tilde{\mu}=\frac{\mu}{T}\frac{\rho_c T_c}{P_c} \tag{1}$$

The fundamental equation for the potential $\tilde{P}$ has the form

$$\tilde{P}=\Delta\tilde{P}+1+\Delta\tilde{\mu}+\tilde{P}_{11}\,\Delta\tilde{\mu}\,\Delta\tilde{T}+\tilde{P}_0(\Delta\tilde{T}) \tag{2}$$

with

$$\Delta\tilde{T}=\tilde{T}+1, \qquad \Delta\tilde{\mu}=\tilde{\mu}-\tilde{\mu}_0(\Delta\tilde{T}) \tag{3}$$

where $P_0(\Delta\tilde{T})$ and $\tilde{\mu}_0(\Delta\tilde{T})$ are analytic functions represented by truncated Taylor expansions,

$$\tilde{P}_0(\Delta\tilde{T})=\sum_{j=1}^{3}\tilde{P}_j(\Delta\tilde{T})^j \tag{4}$$

$$\tilde{\mu}_0(\Delta\tilde{T})=\tilde{\mu}_c+\sum_{j=1}^{3}\tilde{\mu}_j(\Delta\tilde{T})^j \tag{5}$$

The scaled equation for the singular part $\Delta\tilde{P}(\Delta\tilde{\mu}, \Delta\tilde{T})$ of the potential $\tilde{P}$ is specified by the parametric equations,

$$\Delta\tilde{\mu} = r^{\beta\delta}a\theta(1-\theta^2) \tag{6}$$

$$\Delta\tilde{T} = r(1-b^2\theta^2) - cr^{\beta\delta}a\theta(1-\theta^2) \tag{7}$$

$$\Delta\tilde{P} = r^{\beta(\delta+1)}a[k_0 p_0(\theta) + r^{\Delta}k_1 p_1(\theta)] \tag{8}$$

with

$$p_i(\theta) = p_{0i} + p_{2i}\theta^2 + p_{4i}\theta^4 \tag{9}$$

Equations (6) and (7) define a transformation from the physical variables $\Delta\tilde{\mu}$ and $\Delta\tilde{T}$ to the parametric variables r and θ, where r is a measure of the distance from the critical point and θ determines the location on a contour of constant r such that $\theta = \pm 1$ correspond to the two branches of the coexistence curve [19]. Explicit expressions for the various thermodynamic properties derived from this potential can be found elsewhere [14, 18, 20].

The critical exponents β, δ, and Δ and the coefficients b, p_{0i}, p_{2i}, and p_{4i} are universal constants given in Table I. The values adopted for these universal constants are the same as those used in previous publications [4, 14, 20]. The scaling-field amplitudes a, k_0, k_1, and c, the pressure background coefficients $\tilde{P}_{11}$, $\tilde{P}_1$, $\tilde{P}_2$, and $\tilde{P}_3$, and the caloric background coefficients $\tilde{\mu}_c$, $\tilde{\mu}_1$, $\tilde{\mu}_2$, and $\tilde{\mu}_3$ depend on the fluid. The values of these system-dependent constants for methane are presented in Table II.

3. EQUATION OF STATE

The critical-point parameters T_c, P_c, and ρ_c, the scaling-field parameters a, k_0, k_1, and c, and the pressure background parameters $\tilde{P}_1$, $\tilde{P}_2$, $\tilde{P}_3$,

Table I. Universal Constants for the Scaled Fundamental Equation

$\beta = 0.325$
$\delta = 4.82$
$\Delta = 0.50$
$b^2 = 1.3757$
$p_{00} = 0.586535$
$p_{20} = -1.026243$
$p_{40} = 0.612903$
$p_{01} = 0.10325$
$p_{21} = 0.16032$
$p_{41} = -0.16986$

Table II. Critical-Region Constants for Methane

Critical-point parameters	$T_c = 190.551$ K
	$P_c = 4.5992$ MPa
	$\rho_c = 162.66\ \mathrm{kg \cdot m^{-3}}$
Scaling-field parameters	$a = 17.734$
	$k_0 = 1.0796$
	$k_1 = 0.4950$
	$c = -0.007784$
Pressure background parameters	$\tilde{P}_1 = 4.9797$
	$\tilde{P}_2 = -16.712$
	$\tilde{P}_3 = 4.8166$
	$P_{11} = -0.17078$
Caloric background parameters	$\tilde{\mu}_c = 10.214$
	$\tilde{\mu}_1 = 23.519$
	$\tilde{\mu}_2 = -10.305$
	$\tilde{\mu}_3 = -2.5272$

and $\tilde{P}_{11}$ specify the relationship among pressure, density, and temperature. Accurate experimental P–ρ–T data for methane near the critical point have been reported by Kleinrahm et al. [9, 10]. From an analysis of the coexisting vapor and liquid densities and the saturation pressures, Kleinrahm and Wagner [9] obtained for the critical parameters

$$\begin{aligned} T_c &= (190.551 \pm 0.010)\ \mathrm{K} \\ P_c &= (4.5992 \pm 0.0020)\ \mathrm{MPa} \\ \rho_c &= (162.66 \pm 0.05)\ \mathrm{kg \cdot m^{-3}} \end{aligned} \tag{10}$$

In determining the constants of the scaled equation of state, it is possible to treat the critical parameters as adjustable parameters. Varying the critical parameters, however, did not lead to any further improvements and we retained the critical-parameter values, given by Eq. (10), reported by Kleinrahm and Wagner.

As a first step, we determined the scaling-field parameters and the pressure background parameters from the experimental $P - \rho - T$ data of Kleinrahm et al. [9, 10], obtaining

$$\begin{aligned} &a = 17.662, \quad k_0 = 1.0821, \quad k_1 = 0.47911, \quad c = 0.007588 \\ &\tilde{P}_1 = 4.9853, \quad \tilde{P}_2 = -16.313, \quad \tilde{P}_3 = 0, \quad \tilde{P}_{11} = -0.17631 \end{aligned} \tag{11}$$

Our scaled equation of state represents the data of Kleinrahm et al. for $r \leqslant 0.065$ with a weighted standard χ^2 of 0.09; this small value of χ^2

indicates that the statistical errors are smaller than the physical errors reported by Kleinrahm et al. [9, 10]. The coefficient $\tilde{P}_3$ was found to be insignificant. The reason is that the experimental data of Kleinrahm et al. do not extend beyond 193 K, with is only 2.5 K above the critical temperature.

To extend the scaled equation of state to higher temperatures, we need to consider additional P–ρ–T data. The experimental P–ρ–T data reported

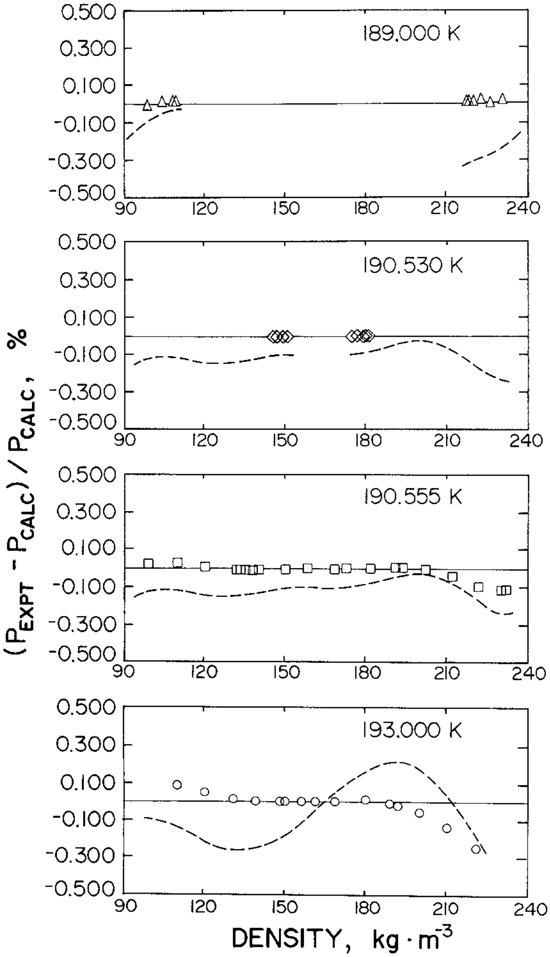

Fig. 1. Percentage differences between the experimental pressure data of Kleinrahm et al. [10] and the values calculated from the scaled fundamental equation. The dashed curves correspond to pressures calculated from the IUPAC formulation.

earlier by Jansoone et al [21] are not suitable for this purpose since they do not cover a larger range of temperatures and densities. The experimental P–ρ–T data reported by Vennix et al. [22] do extend to higher temperatures. It is possible to represent the data of Vennix et al. in the critical region with our scaled equation of state, but the critical pressure implied by these data was found to be about 0.0055 MPa lower than that implied by the vapor pressure data of Kleinrahm and Wagner, indicating an inconsistency between the two data sets. As an alternative, we generated calculated P–ρ–T data at higher temperatures from the international formulation issued by IUPAC [3]. This procedure has the added advantage that the scaled equation of state will connect more smoothly with the IUPAC formulation at higher temperatures. By including P–ρ–T data calculated from the IUPAC equation at temperatures between 200 and 208 K (200 K being the lowest temperature where the IUPAC formulation is judged to be reliable), we obtained the scaling-field and pressure background parameters listed in Table II. The values are quite similar to the values given by Eq. (11) deduced from the data of Kleinrahm et al. alone except that the coefficient $\tilde{P}_3$ has now become significant. With the parameter values in Table II the weighted standard χ^2 for the data of Kleinrahm et al. increases only from 0.09 to 0.10.

A comparison of our scaled equation of state with the P–ρ–T data of Kleinrahm et al [10] is presented in Fig. 1, and a comparison with the vapor pressure data of Kleinrahm and Wagner in Fig. 2. In the same figures we have include a comparison with the pressures calculated from the IUPAC formulation [3]. Within its range of validity (to be discussed

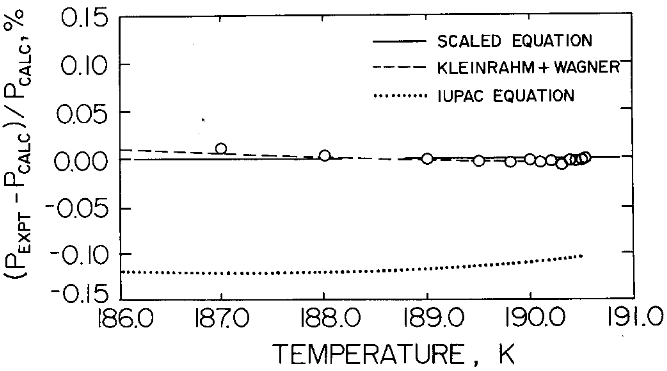

Fig. 2. Percentage differences between the experimental vapor pressures of Kleinrahm and Wagner [9] and the values calculated from the scaled fundamental equation. The dotted curve represents the IUPAC formulation and the dashed curve represents the vapor pressures calculated from the equation of Kleinrahm and Wagner.

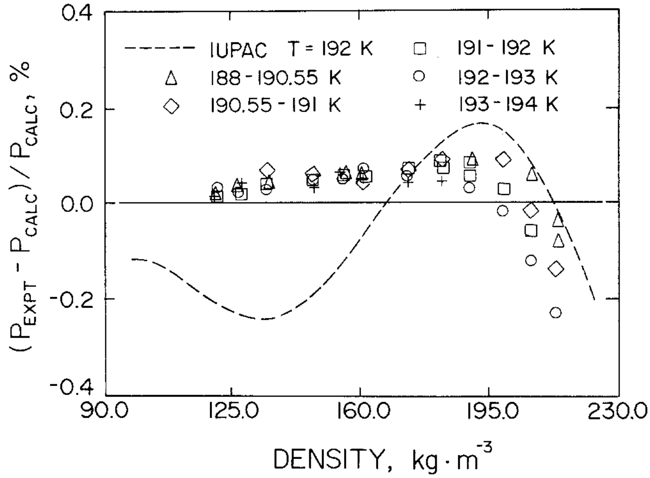

Fig. 3. Percentage differences between the experimental pressure data of Jansoone et al. [21] and the values calculated from the scaled equation. The dashed curve corresponds to pressures calculated from the IUPAC formulation.

below), the scaled equation reproduces the pressure data of Kleinrahm et al. with a standard deviation of 0.025% and the vapor pressure data with a standard deviation of 0.005%. The IUPAC formulation yields a standard deviation for the pressure data as large as 0.16%. A comparison of our scaled equation of state with the P–ρ–T data of Jansoone et al. [21] is shown in Fig. 3. Our scaled equation of state reproduces the pressures of Jansoone et al. with a standard deviation of 0.1%, while the IUPAC formulation yields a standard deviation of 0.2%. In the liquid state at $\rho = 240\ \mathrm{kg \cdot m^{-3}}$, our scaled equation begins to develop some systematic deviations.

4. CALORIC PROPERTIES

The coefficients $\tilde{\mu}_2$ and $\tilde{\mu}_3$ specify the analytic background to the specific heat and they were determined from a fit to the new sound-velocity data of Sivaraman and Gammon [11]. Problems were encountered with the sound-velocity data near saturation and at $T = 190.56$ K in the density range from 160 to $180\ \mathrm{kg \cdot m^{-3}}$. We attributed these problems to an inconsistency between the coexistence boundary of Kleinrahm and Wagner [9] and that implied by the sound-velocity data of Sivaraman and Gammon. In determining $\tilde{\mu}_2$ and $\tilde{\mu}_3$ we omitted these data. With error estimates of 0.001 K in temperature, 0.005 MPa in pressure, and 1% in the speed of sound C_s, the scaled fundamental equations fits the remaining sound-velocity data with a weighted standard χ^2 of 1.2.

A comparison between the scaled fundamental equation and the experimental sound-velocity of Gammon et al. [11, 12] is presented in Fig. 4. The scaled fundamental equation reproduces the sound-velocity data in the critical region with a standard deviation of 2.9%. When the sound velocities are calculated from the IUPAC formulation, the corresponding standard deviation is 14%. The problem is that in the IUPAC formulation, C_s does not vanish at the critical point but reaches a finite value of about 258 $m \cdot s^{-1}$.

In Fig. 5, we show a comparison with the isochoric specific heat in the one-phase region as measured by Younglove [23] and reevaluated by

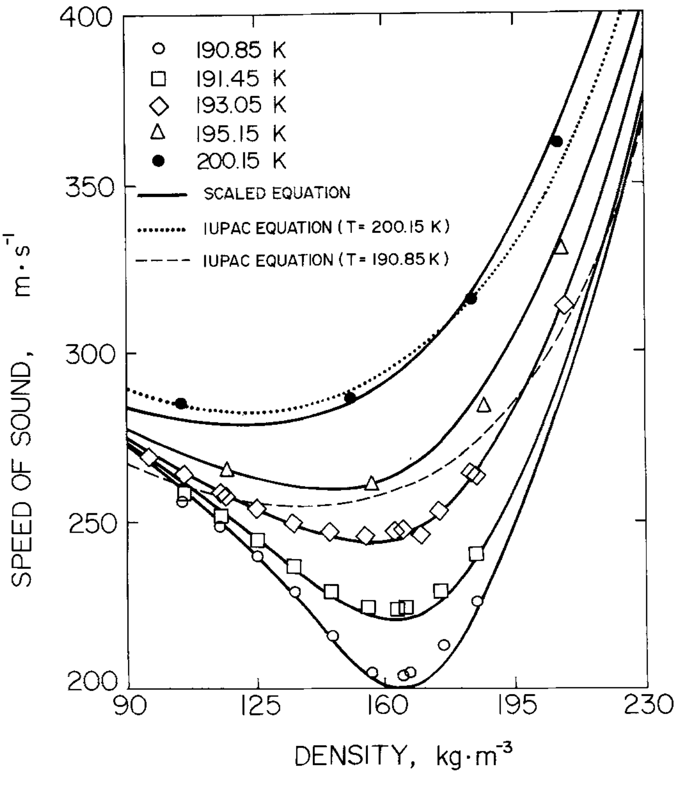

Fig. 4. Sound velocity C_s as a function of density at various temperatures. The data points are experimental values of Gammon et al. [11, 12] and the solid curve represents C_s values calculated from the scaled fundamental equation.

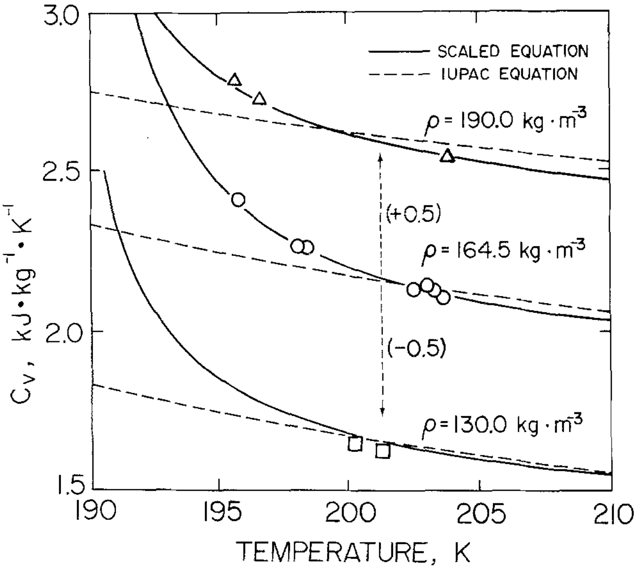

Fig. 5. Specific heat C_v as a function of temperature at various densities. The data points are experimental values of Younglove [23] as corrected by Roder [24], the solid curves represent C_v values calculated from the scaled fundamental equation, and the dashed curves indicate C_v values calculated from the IUPAC formulation. To separate the isochores the C_v scale corresponding to $\rho = 130$ and $190\,\mathrm{kg\cdot m^{-3}}$ has been displaced by -0.5 and $+0.5\,\mathrm{kJ\cdot kg^{-1}\cdot K^{-1}}$, respectively.

Roder [24]. The scaled fundamental equation reproduces these C_v values with a standard deviation of 0.8 %. In the IUPAC formulation C_v does not diverge at the critical point but reaches a maximum value of $2.32\,\mathrm{kJ\cdot kg^{-1}\cdot K^{-1}}$.

5. RANGE OF VALIDITY

The parametric variable r is a measure of the distance to the critical point and the range of validity of the scaled fundamental equation is most directly expressed in terms of this distance variable. Specifically, the scaled fundamental equation is valid for

$$\begin{aligned} r &\leqslant 0.065 \quad \text{at} \quad 187\,\mathrm{K} < T < 195\,\mathrm{K} \\ t &\leqslant 0.085 \quad \text{at} \quad 195\,\mathrm{K} < T < 208\,\mathrm{K} \end{aligned} \tag{12}$$

The corresponding range in the T–ρ plane is shown in Fig. 6. It corresponds approximately to densities from 90 to $230\,\mathrm{kg\cdot m^{-3}}$ at $T = 187\,\mathrm{K}$ to densities from about 130 to $190\,\mathrm{kg\cdot m^{-3}}$ at $T = 205\,\mathrm{K}$. In

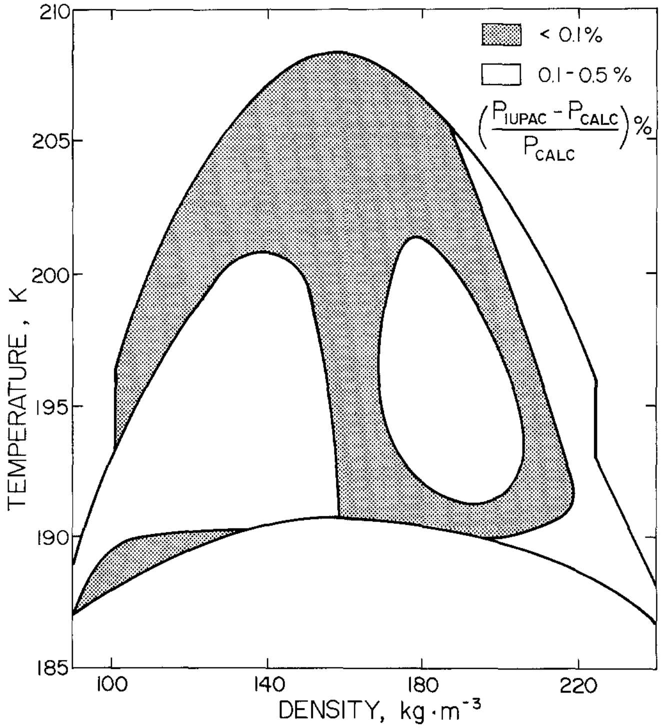

Fig. 6. Range of densities and temperatures for the scaled fundamental equation. In the shaded area the pressures calculated from the scaled fundamental equation and from the IUPAC formulation differ by less than 0.1 %.

Fig. 6, we also indicate where, within this range, the pressures calculated from the scaled fundamental equation and those calculated from the IUPAC formulation differ by less than 0.1 %.

To complete our equation, we need to adopt values for $\tilde{\mu}_c$ and $\tilde{\mu}_1$ which are related to the zero points of entropy and energy. We have determined these constants by identifying the energy and entropy of our surface at $T = 205.89$ K and $\rho = 155.0\ \mathrm{kg \cdot m^{-3}}$ with the energy and entropy of the IUPAC formulation [3]. At this matching point the difference in the pressures calculated from the two equations is 0.0002 % and the difference in the calculated sound velocities is 0.009 %.

Unfortunately, the range of validity of our scaled equation is not large enough to accomplish a smooth connection with the global IUPAC formulation. Specifically, at temperatures below 200 K, there are ranges of densities where neither the scaled fundamental equation nor the IUPAC formulation yields a satisfactory representation of the thermodynamic surface. To solve this problem we need to develop a fundamental equation that incorporates the crossover from the singular scaled behavior near the critical point to the classical analytic behavior far away from the critical point [4, 25]. Such research is in progress [26].

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