

# Thermophysical Properties of Methane: Orthobaric Densities and Some Thermal Properties\*

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For use in the computation of thermodynamic functions, analytical descriptions are given for the following properties: the orthobaric densities and saturation temperatures; the heats of vaporization; the specific heats of saturated liquid; and the thermodynamic functions for ideal gas states.

Key words: Heats of vaporization; methane; orthobaric densities; specific heats of the saturated liquid; thermofunctions for ideal gas states; thermophysical properties.

## List of Symbols

Subscripts *c* and *t* refer to critical and liquid triple points.

Subscripts *g* and *l* refer to vapor and liquid in equilibrium.

*a, b, c*, constant coefficients  
*A<sub>i</sub>*, constant coefficients  
*β*, an exponent, 0.36  
*C<sub>v</sub>*, molal heat capacity at constant volume  
*C<sub>p</sub>*, molal heat capacity at constant pressure  
*C<sub>σ</sub>*, molal heat capacity of saturated liquid  
*d*, molal density  
*Δ*, any relative deviation,  $(y/y_{\text{calc}}-1)$   
*E*, the internal energy  
*ε*, exponent in various expressions  
*H*, the enthalpy  
*J*, the joule  
*k*, conversion factor, 101.325 J/l-atm  
*l*, the liter, 1000 cm<sup>3</sup>  
mol, 16.042 grams of methane  
*P*, pressure, 1 atm = 101325 N/m<sup>2</sup>  
 $\Phi(T)$ ,  $(E^0 - E_0^0)/RT$ , internal energy function  
*Q<sub>r</sub>*, heat absorbed in a reversible change of state  
*R*, the gas constant, 8.3143 J/(mol·K), [26]  
*ρ*, *d/d<sub>t</sub>*, density reduced at *d<sub>t</sub>*  
*S*, the entropy  
*σ*, *d/d<sub>c</sub>*, density reduced at *d<sub>c</sub>*  
*T*, temperature, K, IPTS (1968)  
*T<sub>s</sub>(ρ)*, liquid-vapor coexistence temperature  
*τ*, *T/T<sub>c</sub>*, temperature reduced at *T<sub>c</sub>*  
*u*,  $(T_c - T)/(T_c - T_t)$ , normalized temperature, origin at *T<sub>c</sub>*

*v*, 1/*d*, molal volume  
*w*,  $(T_c/T - 1)/(T_c/T_t - 1)$ , inverse normal temp., origin at *T<sub>c</sub>*  
*ω*,  $\epsilon/x$ , an argument in eq (8)  
*x*, *T/400*, reduced temperature for eq (8)  
*Y*, function of *C<sub>σ</sub>*, defined on figure 5  
*z*,  $(1 - \tau)$ , reduced temperature with origin at *T<sub>c</sub>*.

The number of digits, given for coefficients in the empirical functions of this report, is chosen to yield calculated results having at least the same number of figures as exist in the data to be described.

## 1. Introduction

The current need for thermodynamic properties of methane was described in our preceding report [1].<sup>1</sup> The present report concludes our selection of published properties data for coexisting vapor and liquid, and includes also a description of the ideal gas thermofunctions. All of these properties are placed in analytical form directly useful for thermal computations.

Temperatures are on the IPTS (1968), as in [1], and we use the same fixed-point constants: *T<sub>t</sub>* = 90.66 K, *P<sub>t</sub>* = 0.1151 atm, (0.01166 MN/m<sup>2</sup>), *d<sub>t</sub>* = 28.0536 mol/l (liquid); and *T<sub>c</sub>* = 190.53 K, *P<sub>c</sub>* = 45.346 atm, (4.5947 MN/m<sup>2</sup>), *d<sub>c</sub>* = 10.15 mol/l.

## 2. The Orthobaric Densities

For the densities of coexisting vapor and liquid methane the preponderance of published data is on the liquid phase [2, 3, 4, 5, 6, 7, 8]. For the vapor phase, therefore, we have estimated data at densities

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<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

up to 1/3 of  $d_c$  by use of the vapor pressure equation and the virial equation of state. We used the representation of second virial coefficients based on data of Sengers, Klein, and Gallagher, as well as the third virial coefficient, both as described in [1].

Analytical description of the vapor densities is given by our new form, constrained to qualitatively acceptable behavior near the critical point [9]. To facilitate selection of significant figures in the coefficients, we use variables  $u$  and  $w$  normalized to a maximum value of unity (at the triple point: see list of symbols). Vapor densities now are described by use of exponent  $\beta=0.36$ ,

$$\ln(\rho_g/\rho_c) = A_1 \cdot w + A_2 \cdot u^\beta + \sum_{i=3}^8 A_i \cdot u^{i-2}, \quad (1)$$

$$A_1 = -27.42 \quad 792 \quad A_5 = -10.44 \quad 279$$

$$A_2 = -1.56 \quad 983 \quad A_6 = 23.44 \quad 911$$

$$A_3 = 10.16 \quad 428 \quad A_7 = -18.38 \quad 419$$

$$A_4 = 10.16 \quad 575 \quad A_8 = 7.56 \quad 705$$

The value for exponent  $\beta$  was selected by considering the published values,  $\beta=0.367$  [10], and  $\beta=0.3566$  [11]. The number of terms in (1) was selected to bring deviations down to the level of estimated uncertainty in data derived from the vapor pressure and virial equations. Individual relative deviations of vapor densities from eq (1) are plotted on figure 1. The rms deviation for 55 points is 0.21 percent.

Saturated liquid densities are described by our simple form [9] using argument  $z \equiv (1-\tau)$ ,

$$\rho_l/\rho_c - 1 = a \cdot z + b \cdot z^\beta + c \cdot \exp(-\epsilon \cdot \tau^2/z), \quad (2)$$

$$a = 0.62 \quad 253 \quad c = -0.08 \quad 367$$

$$b = 1.89 \quad 542 \quad \epsilon = 0.6$$

Inconsistent data were eliminated successively, leaving 60 points with an rms relative deviation of 0.24 percent. Figure 2 gives individual relative deviations

from eq (2), and identifies the sources. At the triple point 90.66 K, eq (2) gives a liquid density  $d_l = 28.0536$  mol/l resting primarily on the data of [8], as seen on the figure.

Figure 3 gives the coexisting densities of vapor and liquid methane along the abscissa, calculated by eqs (1, 2). The ordinate gives the saturation temperature,  $T_s(\rho)$ . This plot provides a quick, rough estimate of the data. Conspicuously absent is the line for densities of freezing liquid. Some values recently have been estimated to 94.5 K (150 atm), including the volume change and heats of melting [12].

The rectilinear diameter may be derived by use of eqs (1, 2) for interpolation of  $d_g$  and  $d_l$  to the same temperatures. For 39 points at  $112 \leq T \leq 188$  K, our representation in mol/l,

$$(d_g + d_l)/2 = a + b \cdot z + c \cdot \exp(-\epsilon/z), \quad (3)$$

$$a = 10.156, \quad b = 7.209, \quad c = 0.183, \quad \epsilon = 3/4,$$

yields an rms deviation of 0.05 percent and a critical density  $d_c = 10.156 + 0.02$  mol/l, as compared with  $d_c = 10.15$  adopted for present work.

The relation,  $T_s(\rho)$ , is important in the nonanalytic equation of state [13]. For the combined data of figures 1 and 2 we obtain coefficients for the expression,

$$T_c/T_s = 1 + |\sigma - 1|^{3 \cdot F(\rho)}, \quad (4)$$

$$F(\rho) \equiv A_1 \cdot \ln(1/\rho) + \sum_{i=2}^9 A_i \cdot \rho^{i-2},$$

$$A_1 = 0.19 \quad 3073 \quad A_6 = -112.50 \quad 780$$

$$A_2 = -0.34 \quad 282 \quad A_7 = 141.02 \quad 284$$

$$A_3 = 2.44 \quad 483 \quad A_8 = -89.60 \quad 804$$

$$A_4 = -12.24 \quad 696 \quad A_9 = 22.74 \quad 904$$

$$A_5 = 48.68 \quad 975 \quad \text{rms} = 0.20 \%$$

The signs and magnitudes of these coefficients are comparable with values found for other substances [9].

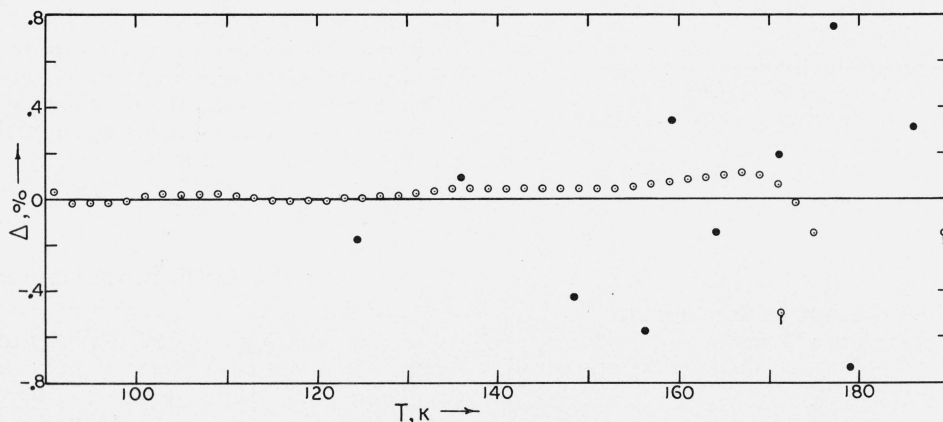


FIGURE 1. Relative deviations of the densities of saturated methane vapor from eq (1).

Open circles from the virial surface and vapor pressures; filled circles from [4]; circles with tails from [5].

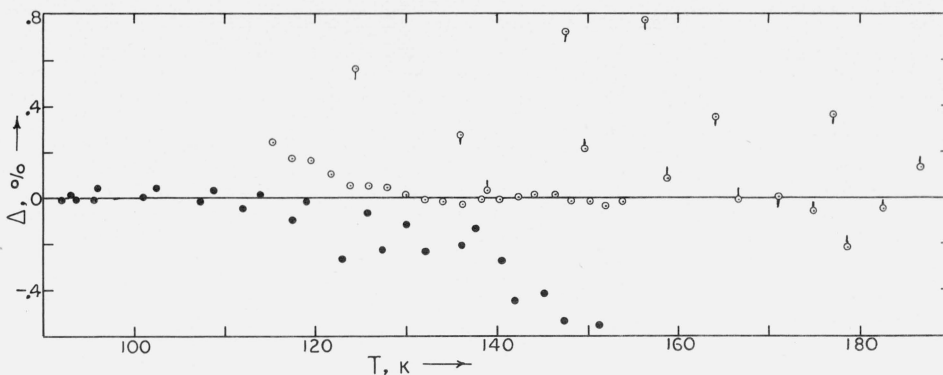


FIGURE 2. Relative deviations of the densities of saturated liquid methane from eq (2).  
Filled circles from [8]; open circles from [7]; tails up from [5]; tails down from [4].

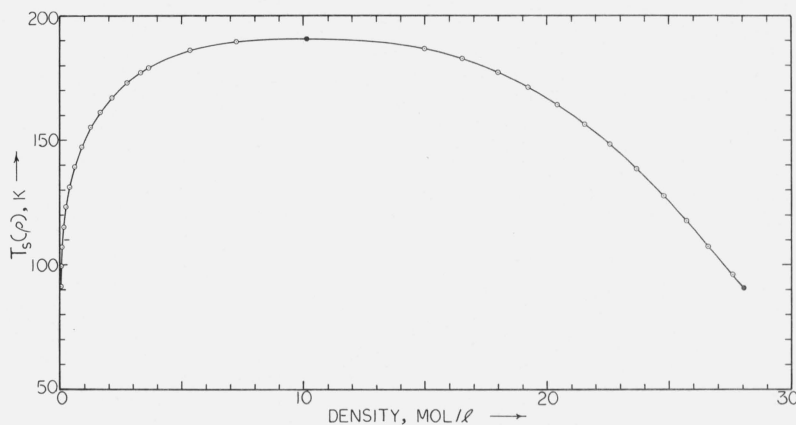


FIGURE 3. Methane saturation temperatures as a function of vapor and liquid densities up to the triple point.

### 3. The Heats of Vaporization

Some data for the heats of vaporization,  $\Delta H_v$ , have been reported [14, 15]. We now use the Clapeyron equation to calculate these heats by use of our vapor pressure equation [1] and eqs (1 and 2) of the present report,

$$\Delta H_v = k \cdot T \cdot (dP/dT) \cdot (v_g - v_l). \quad (5)$$

Column 1 of table 1 gives the same rounded temperatures used in [14, 15]. (Experimental uncertainties do not demand conversion to the IPTS-1968.) Second and third columns of table 1 give the published data in kilo-Joules/mole. The fourth column gives our results via (5). The remaining three columns are the derived data used on the right of (5). Figure 4 gives the outline for our calculated results.

For some computations it would be convenient to use a more direct description of  $\Delta H_v$  than given by (5). For the 21 points in the fourth column of table 1 the following representation gives a maximum relative deviation  $\Delta = -0.04$  percent at 120 K; deviations of 0.00

percent at  $T=185$  and  $T=190$  K; and an rms deviation of 0.02 percent,

$$\Delta H_v = \sum_{i=1}^6 A_i \cdot u^{i/3}, \text{ kJ/mol}, \quad (6)$$

$$\begin{aligned} A_1 &= 7.88860 & A_4 &= -152.63520 \\ A_2 &= -12.94022 & A_5 &= 136.57252 \\ A_3 &= 76.33098 & A_6 &= -46.55421 \end{aligned}$$

### 4. Specific Heats of Saturated Liquid

Specific heats of the liquid phase, along the co-existence path, are useful for computing thermodynamic properties into compressed liquid states. Data for  $C_\sigma$  are derived from observations on the two phase, liquid-vapor system at constant volume by use of accurate PVT data for the two phases [17]. Published data for methane are quite uncertain because the authors failed to give either their experimental observations or a quantitative description of their derivations [14, 15]. The data are shown by figure 5 in

TABLE 1. Heats of vaporization for methane, kJ/mol

T, K	$\Delta H_v$			$dP/dT$ atm/K	$v_g$ l/mol	$v_l$ l/mol
	[14]	[15]	Calc			
90.66			8.661	0.0147	64.1399	0.0356
95.00			8.597	.0227	39.4535	.0361
100.00	8.571	8.494	8.506	.0353	23.8300	.0367
105.00	8.433	8.355	8.394	.0522	15.1377	.0373
110.00	8.300	8.213	8.260	.0741	10.0373	.0379
115.00	8.162	8.063	8.110	.1014	6.9043	.0385
120.00	8.025	7.899	7.943	.1344	4.9011	.0392
125.00	7.878	7.724	7.761	.1734	3.5743	.0400
130.00	7.731	7.531	7.563	.2186	2.6672	.0408
135.00	7.565	7.326	7.347	.2702	2.0295	.0416
140.00	7.394	7.104	7.112	.3283	1.5698	.0425
145.00	7.203	6.862	6.856	.3930	1.2310	.0436
150.00	6.987	6.598	6.578	.4645	0.9763	.0447
155.00	6.740	6.305	6.273	.5431	.7814	.0460
160.00	6.468	5.987	5.937	.6292	.6296	.0475
165.00	6.153	5.619	5.563	.7232	.5093	.0493
170.00	5.784	5.197	5.134	.8262	.4121	.0514
175.00	5.339	4.699	4.623	.9397	.3316	.0542
180.00	4.776	4.021	3.980	1.0664	.2625	.0579
185.00	3.933	3.109	3.088	1.2122	.1995	.0636
190.00		0.782	1.267	1.4059	.1269	.0801

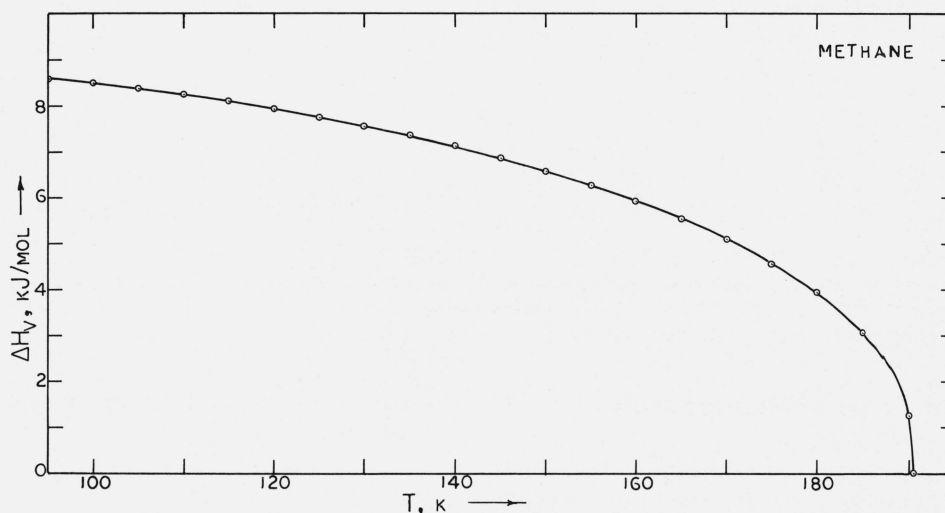


FIGURE 4. Outline for the heats of vaporization of methane, kilo-Joules/mol, derived via the Clapeyron equation with analytical descriptions of the physical properties.

coordinates  $C_\sigma \cdot u^\epsilon$  versus  $T$ , the weighted form used for least squares determination of coefficients in

$$C_\sigma = a + b \cdot u + c/u^\epsilon, \text{ J/(mol K)}, \quad (7)$$

$$a = 29.250 \quad c = 18.924$$

$$b = 5.560 \quad \epsilon = 0.55$$

The value for exponent  $\epsilon$  was selected by analogy: our oxygen data yield  $\epsilon = 0.54$  by trial, and our fluorine data give  $\epsilon = 0.59$  [18]. Present methane data yield  $\epsilon = 1.0 \pm 0.1$ . The line on figure 5 is calculated from

(7). The rms relative deviation is 2.6 percent for 33 values of  $C_\sigma$ .

## 5. The Ideal Gas States

Thermodynamic functions for hypothetical ideal gas states at one atmosphere pressure may be derived for simple molecules as a function of temperature from spectroscopic data by statistical methods [19, 20]. For our thermodynamic computations with PVT data, these ideal gas functions are invaluable because their

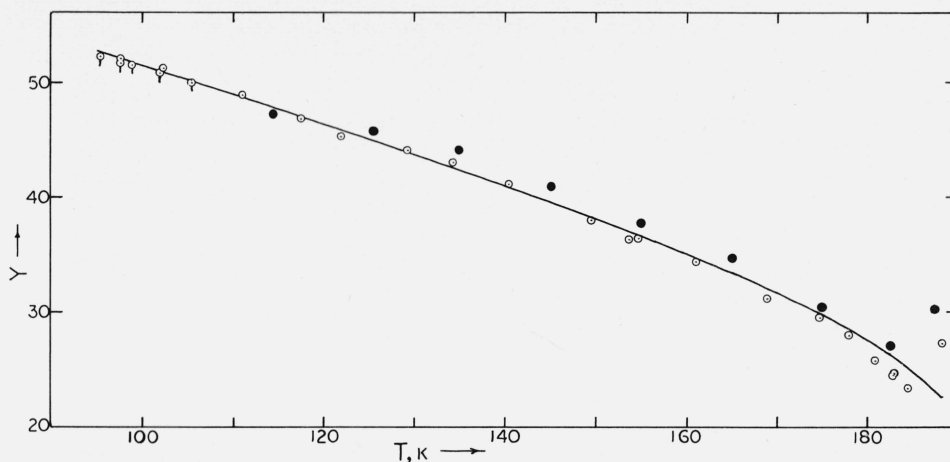


FIGURE 5. The function  $Y \equiv C_r \cdot u^{0.55}$  (J/mol deg) for specific heat of liquid methane along the saturation path, using  $u \equiv (T_c - T)/(T_c - T_1)$ .

Filled circles are from [15]; open circles from [14]; circles with tails from [16]. The line is calculated with eq (7).

accuracy exceeds that which can be attained by experimental specific heat measurements.

Data for methane first were derived in API Project 44 [21], and work to 1961 has been reviewed [22]. For present work we select the recent results of McDowell and Kruse [23], and give them an analytical representation in the range  $60 \leq T \leq 400$  K. With conventional notation [19], abbreviate the internal energy function by  $\Phi(T) \equiv (E^0 - E_0^0)/RT$ , and define the argument  $x \equiv T/400$  with maximum value of about unity for our range of  $T$ .

A formulation with six constants was used for nitrogen [24]. For methane [23] and for oxygen [25] it does not give a highly precise representation of the specific heats. A more precise description is obtained with the power series,

$$\Phi(T) = \sum_{i=1}^{10} A_i \cdot x^{i-1}.$$

On the other hand, a modification of the form given in [24] diminishes specific heat rms deviations by a factor of about 1/2. Maximum deviations in  $C_v^0/R$  (given below) become 0.02 percent in our present range of interest for methane,  $80 \leq T \leq 360$  K. This accuracy is at least an order of magnitude better than can be obtained from PVT data when using the thermodynamic computation,

$$C_r(\rho, T) = C_r^0(T) - T \cdot \int_0^\rho (\partial^2 P / \partial T^2) \cdot d\rho / \rho^2.$$

The modified form (8) uses an argument,  $\omega \equiv \epsilon/x$ . Constant  $\epsilon$  is found by trial,

$$\Phi(T) = A_1 + A_2 \cdot x^{1/3} + A_3 \cdot x^{2/3} + A_4 \cdot x + A_5 \cdot \omega / (e^\omega - 1), \quad (8)$$

$$\begin{aligned} \epsilon &= 5.022\ 880 & A_3 &= -1.847\ 272 \\ A_1 &= 2.599\ 898 & A_4 &= 0.821\ 122 \\ A_2 &= 1.444\ 942 & A_5 &= 4.720\ 791. \end{aligned}$$

The specific heat is obtained via  $C_v^0 = dE^0/dT$ ,

$$C_v^0/R = A_1 + \frac{4}{3} \cdot A_2 \cdot x^{1/3} + \frac{5}{3} \cdot A_3 \cdot x^{2/3} + 2 \cdot A_4 \cdot x + A_5 \cdot [\omega / (e^\omega - 1)]^2 \cdot e^\omega. \quad (9)$$

The entropy is obtained via its definition,

$$\Delta S \equiv Q_r/T = \int_{T_1}^T [C_v \cdot dT/T + P \cdot dv/T].$$

Introducing the published value of  $S^0/R$  at  $T_1 = 60$  K yields,

$$S^0/R = A_0 + \ln(T/60) + A_1 \cdot \ln(x) + 4 \cdot A_2 \cdot x^{1/3} + \frac{5}{2} \cdot A_3 \cdot x^{2/3} + 2 \cdot A_4 \cdot x + A_5 \cdot [\omega / (e^\omega - 1) - \ln(1 - e^{-\omega})] \quad (10)$$

with constant  $A_0 = 18.852\ 484$ .

Specific heat at constant pressure, and the enthalpy function now are simply

$$C_p^0/R = 1 + C_v^0/R, \quad (11)$$

$$(H^0 - E_0^0)/RT = 1 + \Phi(T). \quad (12)$$

Table 2 gives temperatures in the first column. The next three pairs of columns give data and calculated values for  $\Phi(T)$ , for  $C_v^0/R$ , and for  $S^0/R$ .

Independent computations of above data by Harrison et al. [27] give almost identical results at  $90 \leq T < 800$  K, further increasing confidence in their accuracy.

TABLE 2. *Ideal gas functions for methane at 1 atm*

<i>T</i> , K	$\Phi(T)$	Calc	<i>C<sub>v</sub></i> /R	Calc	<i>S<sup>o</sup></i> /R	Calc
60.00	2.9693	2.9693	3.0014	3.0007	15.9337	15.9337
80.00	2.9774	2.9774	3.0019	3.0021	17.0849	17.0849
90.67	2.9803	2.9803	3.0021	3.0023	17.5859	17.5859
100.00	2.9823	2.9823	3.0024	3.0023	17.9779	17.9779
111.67	2.9844	2.9844	3.0027	3.0024	18.4197	18.4197
120.00	2.9857	2.9857	3.0029	3.0026	18.7077	18.7077
140.00	2.9882	2.9882	3.0042	3.0039	19.3248	19.3248
160.00	2.9904	2.9903	3.0075	3.0075	19.8597	19.8596
180.00	2.9927	2.9927	3.0153	3.0157	20.3321	20.3320
200.00	2.9956	2.9957	3.0309	3.0313	20.7559	20.7559
220.00	3.0000	3.0000	3.0571	3.0574	21.1412	21.1412
240.00	3.0063	3.0063	3.0966	3.0966	21.4958	21.4958
260.00	3.0152	3.0152	3.1506	3.1503	21.8257	21.8258
273.15	3.0227	3.0228	3.1943	3.1939	22.0316	22.0316
280.00	3.0272	3.0272	3.2196	3.2191	22.1357	22.1358
298.15	3.0412	3.0412	3.2947	3.2942	22.4030	22.4030
300.00	3.0428	3.0427	3.3030	3.3025	22.4296	22.4296
320.00	3.0620	3.0619	3.3996	3.3994	22.7104	22.7103
340.00	3.0850	3.0849	3.5077	3.5080	22.9803	22.9802
360.00	3.1117	3.1117	3.6257	3.6264	23.2412	23.2412
380.00	3.1420	3.1421	3.7516	3.7527	23.4947	23.4947
400.00	3.1758	3.1759	3.8839	3.8847	23.7417	23.7418
450.00	3.2737	3.2737	4.2328	4.2291	24.3369	24.3369

## 6. Discussion

This report gives analytical descriptions of some methane properties, using existing and estimated data, as a base for preliminary computations of thermodynamic functions over the wide range from gaseous to compressed liquid states at low temperatures. It reveals deficiencies in the quantity of data available for densities of saturated vapor; in the precision of data available for saturated liquid densities; and hence uncertainty, difficult to assess, in the derived heats of vaporization. Data available for specific heats of liquid at coexistence cannot be assessed, due to a lack of published information. For thermofunctions in ideal gas states, the high quality of results derived by McDowell and Kruse suggests that they will stand for a long time.

This laboratory is undertaking an experimental program to obtain reliable and self-consistent measurements over a wide range of conditions and to compute thermodynamic properties based on their formulations.

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