

THE REVIEW OF PHYSICAL CHEMISTRY OF JAPAN, VOL. 42, No. 2, 1972

THERMODYNAMIC PROPERTIES OF GASEOUS METHANE†

BY ICHIMATSU TANISHITA*, KOICHI WATANABE**, HIROSHI KONDO***
AND ATSUSHI NAKASHIMA****

Based upon the most probable values of the compressibility factor for gaseous methane proposed by the High Pressure Data Center of Japan (HPDCJ), the Society of Material Science Japan, a new formulation of the equation of state was devised for the ranges of temperatures between 0 and 225°C and of pressures up to 350 atm. The computed results of the compressibility factor obtained by this new equation of state were then compared with those of available experimental data to evaluate the existing thermodynamic properties data of this substance.

Additionally, the specific volume, the specific enthalpy, the specific entropy and the isobaric specific heat capacity were also calculated using the present formulation established.

Introduction

As is well known, methane is one of the most important substances among the various kinds of hydrocarbons which are currently utilized in modern chemical industry and technology. Therefore, it becomes necessary and important to collect an enough amount of knowledge for the thermophysical properties of gaseous methane which should have sufficient accuracy in case of designing the chemical processes and equipments under the extreme conditions.

Hence, the High Pressure Data Center of Japan (HPDCJ) has nominated working committee***** for the compilation and evaluation of the thermophysical properties data of various important hydrocarbons since 1970 with the sponsorship of the Agency of Science and Technology. This working committee has worked on the compilation and evaluation of the available compressibility factor data for gaseous methane as its first project and then the skeleton table values of the most probable com-

(Received November 28, 1972)

† Part of this paper was read at the 14th High Pressure Conference of Japan, Oct. 23~25, 1972, in Osaka.

* Faculty of Engineering, Nihon University

** Faculty of Engineering, Keio University

*** Fujinetsugaku-kogyo Co., Ltd., Osaka

**** Graduate School of Engineering, Keio University

***** Members of this working committee:

Jiro Osugi (Chief)	Kyoto University,	Yoshimasa Takezaki	Kyoto University,
Tadashi Makita	Kobe University,	Ichimatsu Tanishita	Nihon University,
Hiroji Iwasaki	Tohoku University		

Cooperated with following members:

Koichi Watanabe	Keio University,	Akira Nagashima	Keio University,
Shinji Takahashi	Tohoku University,	Kaoru Date	Tohoku University

compressibility factor for this substance were proposed recently¹⁾.

In cooperation with this project, the authors have started the analytical study for the establishment of the formulations of the thermodynamic properties of gaseous methane in order to make it convenient for the practical applications to chemical industry and technology. Therefore, the thermodynamic properties including calorimetric properties of gaseous methane for the ranges of temperatures between 0 and 225°C and pressures up to 350 atm could be revealed, as is described in details in the present paper.

Basic Data Source Used

The working committee of the HPDCJ described above had searched out systematically almost all of the available data for the PVT relations of methane, and chose 9 original experimental works²⁻¹⁰⁾ as the distinguished data source to be evaluated in its project. The process and method of evaluation for these 9 papers were described in details in the previous paper¹⁾, and the most probable values of the compressibility factor were proposed at the respective grid point.

Hence, these skeleton table values of compressibility factor were used as the basic data source in the present study of formulation. But, the highest pressures in the skeleton table are different with respect to each isotherm and this is not a convenient fact to get the accurate formulation covering the whole ranges of parameters up to 600 atm. Accordingly, we decided to devise the formulation for the ranges of state parameters described above and also utilized several graphically interpolated values only along 25°C isotherm besides these skeleton table values.

Formulated Equation of State

Taking into consideration the convenience and easiness for the practical application, the compressibility factor $Z = Pv/(RT)$ is expressed as a function of pressure P and temperature T , i.e., $Z = Z(P, T)$. The basic functional form of the established equation of state was determined after working out to find several possible functional forms by applying the least squares procedure with the aid of an electronic computer. In this procedure of preliminary consideration, we adopted to use similar functional form of

-
- 1) J. Osugi, Y. Takezaki and T. Makita, *This Journal*, **41**, 60 (1971)
 - 2) F. G. Keyes and H. G. Burks, *J. Am. Chem. Soc.*, **49**, 1403 (1927)
 - 3) H. M. Kvalnes and V. L. Gaddy, *ibid.*, **53**, 394 (1931)
 - 4) A. Michels and G. W. Nederbragt, *Physica*, **2**, 1000 (1935); **3**, 569 (1936)
 - 5) R. H. Olds, H. H. Reamer, B. H. Sage and W. N. Lacey, *Ind. Eng. Chem.*, **35**, 922 (1943)
 - 6) H. W. Schamp, Jr., E. A. Mason, A. C. B. Richardson and A. Altman, *Phys. Fluids*, **1**, 329 (1958)
 - 7) K. Date, G. Kobuya and H. Iwasaki, *Proc. Chem. Res. Inst. Non-Aqueous Solutions*, **10**, 67 (1961)
 - 8) D. R. Douslin, R. H. Harrison, R. T. Moore and J. P. McCullough, *J. Chem. Eng. Data*, **9**, 358 (1964)
 - 9) L. Deffet and F. Ficks, "Advances in Thermophysical Properties at Extreme Temperatures and Pressures", p. 107, ASME, N. Y. (1965)
 - 10) S. L. Robertson and S. E. Babb, Jr., *J. Chem. Phys.*, **51**, 1357 (1969)

equation of state which was previously devised by us for the formulation of the thermodynamic properties of fluorocarbon refrigerant R-22 (difluorochloromethane)^{11,12)}.

Thus, the final form of the established equation of state is determined as the following polynomial form with pressure P .

$$Z = \frac{Pv}{RT} = 1 + \sum_{i=1}^6 \{A_{i0} + A_{i1}/\theta + A_{i2}/\theta^5 + A_{i3} \exp(-5\theta)\} \beta^i, \quad (1)$$

where θ and β are the so-called nondimensional reduced temperature and reduced pressure, defined by T/T_c and P/P_c , respectively. And here T_c and P_c are the critical temperature and the critical pressure for methane adopted as the most suitable values in the present study. The numerical constants including the critical properties are tabulated in Table 1.

Table 1 Numerical constants in Eqs. (1) and (2)

$A_{10} = 0.988087262 \times 10^{-1}$	$A_{40} = -0.253916438 \times 10^{-1}$
$A_{11} = -0.255124704 \times 10^0$	$A_{41} = 0.721976267 \times 10^{-1}$
$A_{12} = 0.124906418 \times 10^0$	$A_{42} = -0.441023599 \times 10^0$
$A_{13} = -0.669677397 \times 10^2$	$A_{43} = 0.664298600 \times 10^2$
$A_{20} = -0.128343854 \times 10^0$	$A_{50} = 0.333739070 \times 10^{-2}$
$A_{21} = 0.366379394 \times 10^0$	$A_{51} = -0.951080464 \times 10^{-2}$
$A_{22} = -0.208751103 \times 10^1$	$A_{52} = 0.584019932 \times 10^{-1}$
$A_{23} = 0.285724445 \times 10^3$	$A_{53} = -0.899333171 \times 10^1$
$A_{30} = 0.857043134 \times 10^{-1}$	$A_{60} = -0.159161534 \times 10^{-3}$
$A_{31} = -0.242998762 \times 10^0$	$A_{61} = 0.454169217 \times 10^{-3}$
$A_{32} = 0.147562337 \times 10^1$	$A_{62} = -0.279911843 \times 10^{-2}$
$A_{33} = -0.212299033 \times 10^3$	$A_{63} = 0.435287250 \times 10^0$
$C_0 = 0.628315913 \times 10^0$	$P_c = 45.80 \text{ atm}$
$C_1 = 0.752532535 \times 10^0$	$v_c = 6.154 \text{ cm}^3/\text{g}$
$C_2 = 0.582779030 \times 10^0$	$T_c = 190.65 \text{ K}$
$C_3 = 0.820437682 \times 10^{-1}$	
$C_4 = -0.107734575 \times 10^{-1}$	

It should be noted that Eq. (1) has the same temperature function in their form for respective pressure term. And it is also self-explanatory that Eq. (1) tends exactly to the ideal gas state of $Z=1$, when both pressure P and density ρ tend to zero at the limit of the ideal gas state.

Correlation of the Isobaric Specific Heat Capacity in the Ideal Gas State

As is well known in the general treatment of the thermodynamic properties derivation, especially

11) I. Tanishita, K. Watanabe, H. Kondo, A. Nakashima and T. Ozawa, "Preprint of the 1972 Annual Meeting of the Japanese Association of Refrigeration", Nov. 7~8, in Tokyo

12) I. Tanishita, K. Watanabe, K. Oguchi and H. Kondo, *Refrigeration*, 47, 24 (1972)

for obtaining the calorimetric properties, it is quite essential to establish the correlation formula of the isobaric specific heat capacity in the ideal gas state C_P^0 . As for the available data source of C_P^0 values for gaseous methane, quite extensive works of compilation, evaluation and correlation have been recently conducted by Makita¹³⁾. Therefore, a new correlation formula for C_P^0 values of gaseous methane was devised by the authors, based upon the set of the most probable C_P^0 values recommended by Makita. This correlation is effective for the range of temperatures between 0 and 225°C and is expressed in a dimensionless form as follows:

$$C_P^0(\theta) = C_0/\theta + C_1 + C_2\theta + C_3\theta^2 + C_4\theta^3, \quad (2)$$

where C_0, C_1, C_2, C_3, C_4 are the numerical constants as given in Table 1.

The maximum and average deviation between the calculated C_P^0 values by Eq. (2) and the recommended values due to Makita were found as 0.057% and 0.026% respectively for the range of temperatures of present interest.

Canonical Function and Derived Functions

The various kinds of thermodynamic properties are not independent of each other. For example, when pressure P and temperature T are chosen as the independent variables of formulation as in the present study, then the expressions (here called derived functions) for the specific volume v , the specific entropy s , the specific enthalpy h and all other thermodynamic properties of the substance may be derived directly by partial differentiation of the so-called canonical (or characteristic) function $g=g(P, T)$, where g is the specific Gibbs free energy. Similarly, when the specific volume v and temperature T are chosen as the independent variables, then the expressions for the pressure P and all other thermodynamic properties may be derived by the similar manner of partial differentiation of the canonical function $f=f(v, T)$, where f is the specific Helmholtz free energy.

Therefore, the formulation of the thermodynamic properties of gaseous methane is then presented in terms of the canonical function $g=g(P, T)$ in its form, thereby maintaining the thermodynamic consistency as well as the practical convenience in the derivation of other important thermodynamic properties. And it should be noted that the canonical function $g=g(P, T)$ provides the definitive expression of the present formulation and that the derived functions such as the specific volume v , the specific entropy s , the specific enthalpy h and the isobaric specific heat capacity C_P are for practical use and are secondary to the canonical function.

If the canonical function of the present formulation is defined as $g=g(P, T)$, then the following derived functions could be easily derived based upon the known general thermodynamic relations

$$\text{specific entropy:} \quad s = -(\partial g / \partial T)_P \quad (3)$$

$$\text{specific volume:} \quad v = +(\partial g / \partial P)_T \quad (4)$$

$$\text{specific enthalpy:} \quad h = g + Ts \quad (5)$$

13) Private communication to the authors

$$\text{isobaric specific heat capacity: } C_P = -T(\partial^2 g / \partial T^2)_P \quad (6)$$

Considering the convenience for the systematic calculation in practical applications, these derived functions given by Eqs. (3)~(6) could be rewritten in the following reduced dimensionless forms with the aid of the definition for the reduced specific Gibbs function as $\zeta = g/(AP_c v_c)$. Here A is a sort of conversion factor and is equal to $9.8692 \text{ atm}^{-1} \cdot \text{J/cm}^3$ in the present study, because the pressure P is in atm, the specific volume v in cm^3/g , temperature T in K, the specific enthalpy h in J/g, specific entropy s and isobaric specific heat capacity C_P are in J/(gK), respectively.

$$\text{reduced specific entropy: } \sigma = s/(AP_c v_c/T_c) = -(\partial \zeta / \partial \theta)_\beta \quad (7)$$

$$\text{reduced specific volume: } \chi = v/v_c = +(\partial \zeta / \partial \beta)_\theta \quad (8)$$

$$\text{reduced specific enthalpy: } \varepsilon = h/(AP_c v_c) = \zeta + \theta \sigma \quad (9)$$

$$\text{reduced isobaric specific heat capacity:}$$

$$\lambda_\beta = C_P/(AP_c v_c/T_c) = -\theta(\partial^2 \zeta / \partial \theta^2)_\beta \quad (10)$$

Therefore, taking into consideration the above definitive expressions of the derived functions, the following reduced specific Gibbs function could be obtained from Eqs. (1) and (2).

$$\begin{aligned} \zeta = & (T_c/AP_c v_c) \{ (C_0 - C_1 \theta) \ln(\theta/\theta_0) + \{ C_0 - C_1 \theta_0 - (C_2 \theta_0^2/2) - (C_3 \theta_0^3/3) - (C_4 \theta_0^4/4) \} \\ & + \theta \{ -(C_0/\theta_0) + C_1 + C_2 \theta_0 + (C_3 \theta_0^2/2) + (C_4 \theta_0^3/3) \} \\ & - (\theta^2/2) \{ C_2 + (C_3 \theta/3) + (C_4 \theta^2/6) \} \} + \left[\sum_{i=1}^6 \{ A_{i0} \theta + A_{i1} + (A_{i2}/\theta^i) + A_{i3} \theta \exp(-5\theta) \} \right. \\ & \left. \times (\beta^i/i) + \theta(\ln P_c + \ln \beta) \right] / Z_c \end{aligned} \quad (11)$$

Calculated Thermodynamic Properties

Using the established equation of state for gaseous methane given by Eq. (1), the compressibility factor Z at each grid point in the skeleton table of the most probable Z values proposed by Osugi *et al.*¹⁾ were calculated with an electronic computer. These results obtained are tabulated in Table 2 with those of the most probable Z values. It is clear that the present computed results are quite satisfactory in their coincidence with the most probable compressibility factor values, even considering the standard deviation estimated in the previous paper¹⁾.

Besides the comparison of Z with the most probable values, the compressibility factor Z corresponding to respective data point of available 9 data sources already mentioned were also calculated in order to compare the computed Z values (Z_{calc}) directly with available experimental data reported in the original papers. In Figs. 1~3, the comparison of Z_{calc} values with respective Z values, including the most probable compressibility factor values, are shown in percentage deviation for three different typical isotherms given in the skeleton table by the previous work.

From the direct comparison of Z_{calc} values with available experimental data values, it becomes clear that the present formulated equation of state for gaseous methane is quite in satisfactory agree-

Thermodynamic Properties of Gaseous Methane

Table 2 Calculated values of the compressibility factor Z for gaseous methane and their comparison with the skeleton table values

Temperature (°C)	0	25	50	75	100	125	150	175	200	225
Pressure (atm)										
1	0.99759	0.99830	0.99876	0.99908	0.99933	0.99952	0.99968	0.99981	0.99994	1.00004
10	0.97599	0.98291	0.98756	0.99087	0.99336	0.99530	0.99688	0.99819	0.99930	1.00027
20	0.95216	0.96525	0.97467				0.99400			
	0.95211	0.96577	0.97515	0.98192	0.98699	0.99090	0.99399	0.99650	0.99858	1.00033
	5/39	-52/30	-48/32				1/3			
30	0.92859	0.94846	0.96257	0.97292	0.98061	0.98669	0.99135	0.99493		
	0.92835	0.94877	0.96297	0.97326	0.98094	0.98680	0.99138	0.99501	0.99795	1.00036
	24/55	-31/39	-40/38	-34/37	-33/30	-11/19	-3/9	-8/23		
40	0.90514	0.93206	0.95109	0.96476	0.97499	0.98290	0.98899	0.99377	0.99744	1.00034
	0.90483	0.93211	0.95116	0.96498	0.97526	0.98304	0.98904	0.99374	0.99748	1.00051
	31/94	-5/46	-7/42	-22/43	-27/29	-14/25	-5/13	3/30	-4/25	-17/3
50	0.88210	0.91620	0.94007	0.95710	0.96977	0.97947	0.98696	0.99285	0.99732	1.00087
	0.88174	0.91598	0.93988	0.95718	0.96999	0.97963	0.98701	0.99273	0.99724	1.00084
	36/76	22/48	19/51	-8/44	-22/32	-16/29	-5/17	12/33	8/31	3/12
60	0.85950	0.90101	0.92969	0.94997	0.96498	0.97644	0.98526	0.99218	0.99744	1.00161
	0.85937	0.90057	0.92924	0.94991	0.96516	0.97659	0.98529	0.99200	0.99726	1.00144
	13/71	44/50	45/41	6/40	-18/41	-15/32	-3/21	18/37	18/35	17/21
70	0.83798	0.88650	0.91986	0.94355	0.96065	0.97381	0.98388	0.99177	0.99782	1.00258
	0.83800	0.88607	0.91935	0.94325	0.96081	0.97394	0.98390	0.99152	0.99756	1.00231
	-2/62	43/72	51/37	30/66	-16/51	-13/31	-2/23	25/38	26/41	27/40
80	0.81776	0.87308	0.91080	0.93760	0.95681	0.97159	0.98286	0.99167	0.99843	1.00371
	0.81798	0.87263	0.91028	0.93722	0.95695	0.97168	0.98284	0.99143	0.99814	1.00347
	-22/80	45/88	52/47	38/79	-14/61	-9/39	2/30	24/61	29/50	24/39
90	0.79920	0.86088	0.90259	0.93210	0.95348	0.96977	0.98215	0.99181	0.99927	1.00510
	0.79962	0.86041	0.90212	0.93187	0.95362	0.96984	0.98213	0.99160	0.99901	1.00491
	-42/118	47/57	47/55	23/30	-14/70	-7/41	2/31	21/64	26/54	19/54
100	0.78267	0.84999	0.89529	0.92748	0.95065	0.96839	0.98174	0.99227	1.00033	1.00664
	0.78323	0.84954	0.89492	0.92722	0.95082	0.96842	0.98177	0.99207	1.00015	1.00660
	-56/170	45/48	37/68	26/41	-17/75	-3/47	-3/30	20/85	18/57	4/52
120	0.75693	0.83236	0.88361	0.92011	0.94666	0.96687	0.98212	0.99398	1.00320	1.01040
	0.75740	0.83225	0.88354	0.92010	0.94687	0.96688	0.98211	0.99391	1.00320	1.01064
	-47/251	11/73	7/69	1/36	-21/72	-1/48	1/43	7/103	0/84	-24/75
140	0.74244	0.82069	0.87602	0.91592	0.94490	0.96706	0.98379	0.99679	1.00694	1.01494
	0.74207	0.82134	0.87633	0.91593	0.94515	0.96711	0.98388	0.99689	1.00714	1.01535
	37/272	-65/43	-31/99	-1/31	-25/57	-5/41	-9/41	-10/92	-20/92	-41/92
160	0.73870	0.81600	0.87280	0.91469	0.94547	0.96904	0.98686	1.00086	1.01167	1.02021
	0.73787	0.81697	0.87332	0.91472	0.94568	0.96912	0.98706	1.00096	1.01187	1.02056
	83/183	-97/100	-52/81	-3/41	-19/44	-8/39	-20/55	-10/141	-20/137	-35/92
180	0.74544		0.87403	0.91603	0.94827	0.97264	0.99123	1.00580	1.01716	1.02634
	0.74433	0.81892	0.87439	0.91641	0.94841	0.97286	0.99160	1.00607	1.01733	1.02619
	111/173		-36/47	-38/92	-14/40	-22/33	-37/46	-27/76	-17/133	15/143
200	0.75968		0.87913	0.92106	0.95323	0.97799	0.99702	1.01200	1.02366	1.03300
	0.75997	0.82662	0.87933	0.92089	0.95327	0.97826	0.99745	1.01218	1.02352	1.03331
	-29/253		-20/41	17/69	-4/44	-27/38	-43/57	-18/102	14/139	69/110
250			0.90743	0.94395	0.97406	0.99814	1.01661	1.03171	1.04348	1.05285
			0.90653	0.94339	0.97398	0.99834	1.01726	1.03175	1.04277	1.05111
			90/173	56/125	8/18	-20/54	-65/55	-4/42	71/86	174/105
300			0.95080	0.98016	1.00537	1.02663	1.04329	1.05690	1.06780	1.07648
			0.95017	0.97967	1.00516	1.02628	1.04341	1.05718	1.06823	1.07716
			63/48	49/91	21/40	35/49	-12/51	-28/4	-43/37	-68/58
350			1.00319	1.02483	1.04429	1.06146	1.07535	1.08683	1.09593	1.10357
			1.00421	1.02519	1.04437	1.06091	1.07476	1.08624	1.09572	1.10360
			-102/318	-36/176	-8/116	55/52	59/80	59/113	21/24	-3/19

1st line: skeleton table values (Z_{st}), 2nd line: calculated values (Z_{calc}), 3rd line: deviation ($Z_{st}-Z_{calc}$)/(3 × std.dev.)

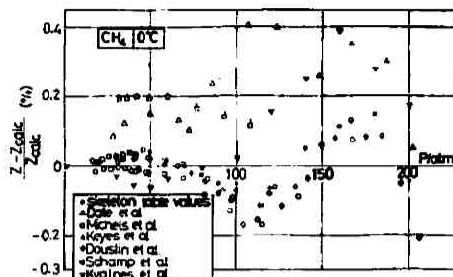


Fig. 1 Comparison of the calculated compressibility factor with the most probable values and with the experimental data along 0°C isotherm

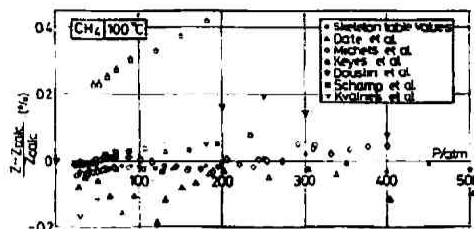


Fig. 2 Comparison of the calculated compressibility factor with the most probable values and with the experimental data along 100°C isotherm

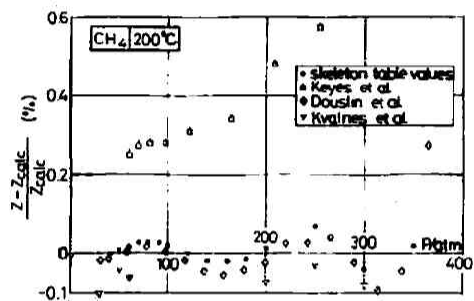


Fig. 3 Comparison of the calculated compressibility factor with the most probable values and with the experimental data along 200°C isotherm

ments with the most probable values of the compressibility factor proposed previously. And among the available PVT experimental data²⁻¹⁰⁾ in the ranges of state parameters of present interest, it is obvious that the best coincidence with the present formulation were obtained for three sets of data^{4,6,8)} which were considered to be the most reliable and the highest weight has been given to in the previous evaluation¹⁾. Next to those three sets of data mentioned above, reasonable agreements with the present formulation were obtained with respect to three other sets of experimental data^{5,7,9)} to which the weight second to the above three sets of data had been given. As for the other two sets of earlier works^{2,3)}, it was found that there exists some considerable amount of discrepancies between their experimental data and the present formulation.

Using Eq. (8) with Eq. (11), the calculations of the specific volume v of gaseous methane were conducted. In Table 3, the calculated results of them are tabulated for respective common temperature and pressure, considering the convenience in practical applications.

The calculation of the calorimetric property values, such as the specific entropy s , the specific enthalpy h and the isobaric specific heat capacity C_p were calculated with the aid of Eqs. (7), (9) and (10), respectively. In case of these calculations of the calorimetric property values, the standard temperature T_0 which is corresponding to $\theta_0 = T_0/T_c$ in Eq. (11) was chosen as 25°C under the atmospheric pressure in accordance with the selected values of the specific entropy and enthalpy recommended by recent NBS compilation¹⁴⁾. The calculated results thus obtained are shown in Figs. 4~6, for the specific

14) D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey and R. H. Schumm, *NBS Tech. Note*, 270-23 (1968)

Thermodynamic Properties of Gaseous Methane

Table 3 Calculated values of the specific volume v (cm³/g) for gaseous methane

Temperature (°C)	Pressure (atm)										
	0	25	50	75	100	125	150	175	200	225	250
1	1393.7	1522.4	1650.8	1779.1	1907.3	2035.5	2163.6	2291.7	2419.9	2548.0	
10	139.15	149.89	163.23	176.44	189.59	202.69	215.76	228.80	241.83	254.86	
20	66.509	73.638	80.588	87.425	94.187	100.90	107.56	114.21	120.83	127.44	
30	43.233	48.228	53.054	57.769	62.406	66.985	71.522	76.025	80.503	84.961	
40	31.603	35.536	39.303	42.958	46.534	50.048	53.515	56.946	60.349	63.730	
50	24.637	27.937	31.069	34.089	37.026	39.899	42.724	45.510	48.267	51.001	
60	20.010	22.889	25.598	28.192	30.701	33.146	35.541	37.897	40.224	42.526	
70	16.725	19.303	21.708	23.995	26.197	28.334	30.421	32.468	34.488	36.483	
80	14.285	16.634	18.807	20.861	22.830	24.735	26.590	28.407	30.194	31.959	
90	12.413	14.579	16.567	18.438	20.223	21.945	23.618	25.255	26.863	28.449	
100	10.942	12.955	14.792	16.511	18.147	19.721	21.249	22.740	24.204	25.647	
120	8.8180	10.576	12.170	13.654	14.901	16.408	17.713	18.985	20.232	21.459	
140	7.4053	8.9465	10.346	11.650	12.885	14.068	15.210	16.322	17.409	18.479	
160	6.4430	7.7866	9.0216	10.180	11.281	12.335	13.352	14.340	15.305	16.252	
180	5.7772	6.9379	8.0290	9.0658	10.056	11.006	11.923	12.812	13.678	14.526	
200	5.3088	6.3028	7.2669	8.1991	9.0969	9.9608	10.794	11.600	12.385	13.151	
250			5.9934	6.7196	7.4356	8.1322	8.8066	9.4598	10.094	10.713	
300			5.2349	5.8150	6.3947	6.9665	7.5275	8.0775	8.6172	9.1484	
350			4.7423	5.2159	5.6950	6.1728	6.6460	7.1139	7.5763	7.0297	

entropy s , the specific enthalpy h and the isobaric specific heat capacity C_P of gaseous methane*), where the temperature was chosen as the parameter. It may be easily understood that the present formulation could satisfactorily reproduce these calorimetric properties tracing after these diagrams. And it is also noteworthy that the isotherm of 250°C could present pretty reasonable tendency in these calorimetric property values, and even it is 25°C beyond the valid temperature range of the present formulation.

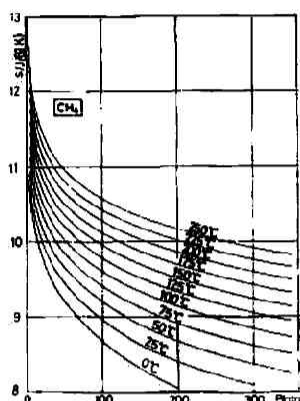


Fig. 4 Calculated specific entropy for gaseous methane

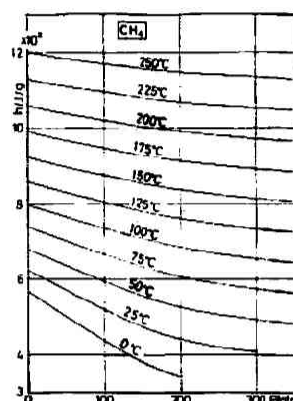


Fig. 5 Calculated specific enthalpy for gaseous methane

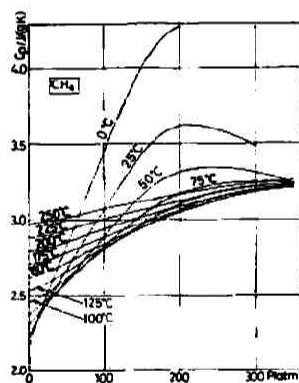


Fig. 6 Calculated isobaric specific heat capacity for gaseous methane

Conclusion

In accordance with the tasks of the compilation, evaluation and dissemination of the thermophysical property data for important hydrocarbons by the working committee of the High Pressure Data Center of Japan, the equation of state for gaseous methane has been formulated for the ranges of temperatures between 0 and 225°C and of pressures up to 350 atm. The basic data source used for the present formulation are the skeleton table values of the most probable compressibility factor adopted by this

*) Calculated results were confirmed being in satisfactory agreements with those given by Din¹⁵⁾.

15) F. Din., ed., "Thermodynamic Functions of Gases", 3, 6, Butterworths (1961)

working committee and reported previously¹⁾.

Using this established formulation, coupled with the new correlation for the isobaric specific heat capacity in the ideal gas state, the compressibility factor, the specific volume, the specific entropy, the specific enthalpy and the isobaric specific heat capacity have been calculated. The obtained results are quite satisfactory for all of these thermodynamic properties of gaseous methane.

Hence most of the essential and fundamental thermodynamic property values for gaseous methane can be revealed thoroughly by the present study for the ranges of state parameters mentioned above and they may be useful in practical applications involving this substance.

Finally, it should be noted that some more extensive experimental works on *PVT* relations for this substance especially in lower temperature regions below 0°C might be necessary and urgent to be conducted in near future, because there exists few reliable experimental data in this region at the present moment.

Acknowledgment

The authors wish to express their sincere appreciation to the members of the working committee of the HPDCJ for their continuous suggestions and encouragements given to the authors.

The authors are so grateful to Prof. T. Makita for his kindness to give the authors his accurate and well-furnished information about C_P° values.

As for the financial support to the present study, the authors are partially indebted to the sponsorship of the Agency of Science and Technology. And one of the authors (K. W.) is also partially supported by the Kawakami Memorial Research Funds for the completion of the present work.