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EVALUATION OF P - V - T RELATIONS

The Most Probable Values of Compressibility Factor of Methane†

BY JIRO OSUGI*, YOSHIMASA TAKEZAKI** AND TADASHI MAKITA***

It is true that no scientific treatment is ever complete as far as its evaluation is made in reference to the previously published reports. It is also necessary to evaluate the previously obtained values not for the emphasis on significance of the author's own experiments, but for the establishment of the scientific data internationally acknowledged. The Committee of High Pressure Data Center of Japan (HPDCJ), the Society of Material Science, Japan, has worked on the evaluation of the compressibility factor of methane with the sponsorship of the Agency of Science and Technology.

The evaluation of P - V - T relations of methane has already been made by Din¹⁾ and Canjor²⁾ who obtained the relations of specific volume or residual volume against pressure. Many papers have been presented for the purpose of obtaining the equation of state, the second virial coefficient or the reduced equation of state from their experimental values which have usually been left unexamined. However, it is difficult to evaluate the original values published which are various in the ranges and scales of experimental conditions.

For the establishment of basic scientific data, it is urgently required to evaluate critically the original values obtained directly from the experiments, independent of theoretical and other modifications.

Upon the considerations mentioned above, the evaluation of the compressibility factor of methane has been worked along the following procedures. The following members of the Committee for the evaluation have been nominated,

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

And the following researchers attended for the discussions,

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

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* Department of Chemistry, Faculty of Science, Kyoto University

** Institute of Chemical Research, Kyoto University

*** Department of Chemical Engineering, Faculty of Engineering, Kobe University

1) F. Din, "Thermodynamic Functions of Gases", Vol. 3, pp. 1~71, Butterworths, London (1961)

2) L. N. Canjor, *Ind. Eng. Chem., Chem. Eng. Data Series*, 3, 185 (1958)

Outline of Processing

The compressibility factor in the expression of P - V - T relations

From the consideration on the techniques used in the determination of P - V - T relation, one of the most favorable expression should be given by the original values of volume/mass (*i.e.* specific volume, or equivalently specific density) obtained directly from the measurements. In this case, the introduction of additional errors resulting from the use of other experimentally determined constants in calculation could be avoided.

However, the figures of specific volume vary in so wide a range according to P and T , and this is inconvenient for the purpose of evaluation which involves the process to examine a number of different measurements over a wide range of P and T .

An alternative expression is $P \times (\text{sp. vol.})$, which is precise as well and free from the above-mentioned fault, but the use of this quantity still has another weak point that the values at a fixed set of P and T changes with the molecular weight of the substance. It is also a shortcoming for the comparison of a variety of substances planned. It has been decided, therefore, to take the molar volume instead of the specific volume from the consideration of the convenience for practical use and of the correlation with the virial expression. To express the PV relative to that of the ideal gas, the compressibility factor has been adopted in the present work.

$$Z = \frac{PV}{RT},$$

where V is the molar volume and R the universal gas constant.

Molecular weight and gas constant

The Committee has decided to adopt the atomic weights recommended by IUPAC (1969)³⁾ in the present work concerning methane: as for C and H necessary for methane, C: $12.011 \pm 0.001^*$ and H: $1.0080 \pm 0.0003^*$. Since 1925 the changes of these atomic weights have been so small that no correction has been needed for the molecular weight of methane given by the authors at the date of issue. Rather, the maximum relative error due to the uncertainties of atomic weights, which amounts to 1.4×10^{-4} for methane, is not well below the experimental errors in the precisest measurements.

As for the universal gas constant, the figure recommended by IUPAC (the 23rd Conference)⁴⁾⁵⁾¹⁰⁾ has been adopted:

$$\begin{aligned} R &= 8.31433 \pm 0.00044 \text{ (J/}^\circ\text{K} \cdot \text{mole)} \\ &= 82.056 \pm 0.004 \text{ (cm}^3 \cdot \text{atm/}^\circ\text{K} \cdot \text{mole)} \end{aligned}$$

* Attached uncertainties are three times the standard deviations.

3) Commission on Atomic Weights, *Pure and Appl. Chem.*, **21**, 95 (1970)

4) M. L. McGlashan, *ibid.*, **21**, 37 (1970)

5) F. R. Rossini, *ibid.*, **9**, 453 (1964)

10) Thermodynamics Research Center Data Project, "Selected Values of Properties of Chemical Compounds", Texas A & M Univ., pp. 11~20 (1966)

The relative uncertainty of Z caused by introducing R amounts to 5.3×10^{-5} , which can be neglected even for the precisest measurements.

Temperature and pressure scales

In the tabulation of Z with respect to the common and fixed points of P and T , which is necessary for the comparison of the data determined by many authors, the following sets of discrete temperatures and pressures have been employed:

Temperature ($^{\circ}\text{C}$ Int, 1948): 0, 25, 50, 75,...225 (interval of 25°C)

Pressure (atm): 1, 3, 5, 10, 20, 30,...100 (interval of 10 atm)

100, 120, 140,...200 (interval of 20 atm)

200, 250, 300,...1000 (interval of 50 atm)

1000, 1200, 1400,...3000 (interval of 200 atm).

The thermodynamic temperature scale should be used as the absolute temperature in the calculation of Z . This conversion has been made according to the international decision in 1948, that is, by

$$T(^{\circ}\text{K therm}) = 273.15 + t(^{\circ}\text{C therm})^6,$$

$$t(^{\circ}\text{C therm}) = t_1(^{\circ}\text{C Int, 1948}) + (0.04106 - 7.363 \times 10^{-5} t_1) \left(\frac{t_1}{100} \right) \left(\frac{t_1}{100} - 1 \right)^2,$$

where $t(^{\circ}\text{C, Int.})$ is the experimental temperatures given in $^{\circ}\text{C}$ in the literatures. No conversion is necessary for the international Celsius temperatures between the scales of 1927 and 1948 in the temperature range processed in this report⁶⁾.

In 1968 the revision of the temperature scale was made⁸⁾, but in consideration of the fact that the new scale is not so prevalently used, especially not legally announced in Japan⁸⁾, it has been decided to use the 1948 scale* for the time being.

The conversion of the temperature given in $^{\circ}\text{F}$ or $^{\circ}\text{R}$ into $T(^{\circ}\text{K therm})$ is made through

$$^{\circ}\text{C (Int)} = \{^{\circ}\text{F (Int)} - 32\} \times \frac{5}{9},$$

$$^{\circ}\text{F (Int)} = ^{\circ}\text{R (Int)} - 459.69.$$

As the unit of pressure, the use of the international unit system (SI Unit)⁹⁾ seems desirable in view of the trends in the scientific fields. However, most of the original determinations have been made in terms of atm unit and many properties other than P - V - T are also determined with atm unit. Therefore, it seems convenient for the moment to use the heretofore commonly used unit in order to connect

* The deviation of IPTS-1948 scale in the thermodynamic temperature from the 1968's is less than 5×10^{-5} between 0 and 160°C and less than 1×10^{-4} for $160 \sim 225^{\circ}\text{C}$ ⁸⁾. These deviations are negligible, comparing with other uncertainties included.

6) J. A. Hall, "Temperature, its Measurements and Control in Science and Industry", Vol. 2, p. 115, ed. by H. C. Woeff, Reinhold, New York (1955)

7) J. A. Beattie, *ibid.*, p. 63 (1955)

8) F. D. Rossini, *Pure and Appl. Chem.*, **22**, 557 (1970); T. Mochizuki, *Keiryō Kenkyūsho Hokoku (Report of the National Research Laboratory of Metrology, Japan)*, **18**, 12 (1969)

9) ref. 4) p. 19 (1970)

these properties. Thus, in compromise of these facts the Committee has settled to prefer atm unit at least for the present work. But, on this point further consideration should be put forward.

Conversion of atm into SI Unit is given by

$$1 \text{ atm} = 1.013250 \text{ bar} = 1.013250 \times 10^5 \text{ N/m}^2 \text{ (exactly by definition)}^{(5)}.$$

Consideration on the purity of sample

The most abundant impurities in methane used are nitrogen and ethane. Though the effect of these impurities on Z is difficult to estimate, a rough calculation shows that maximum relative error is *ca.* 2×10^{-4} for 99.9% purity and that is *ca.* 2×10^{-5} for 99.99%. No correction has been made in the calculation of Z and the considerations on purity have been given together with other factors in the evaluation.

Method of interpolation

In the present evaluation, a number of common temperatures and pressures are specified as mentioned in the preceding sections, in order to compare the available data collected from various sources. When the data reported are not at one of the common temperatures and pressures specified, interpolating procedures should be carried out along an isotherm or an isobar on a digital computer using an appropriate program designed by the HPDCJ.

The original data points along an isotherm have been fitted to several equations by the least squares method. If necessary, one isotherm has been divided into two or three sections in order to obtain the standard deviations less than the experimental errors reported by the original authors. In many cases, cubic or quartic equations of pressure are found to be satisfactory for the present interpolation. When the original data were reported at temperatures other than the specified common temperatures, the same procedures of interpolation have been performed along an isobar of common pressure. The cubic equations of the reciprocal temperature are found to be excellent to reproduce the original data within the reported errors.

Procedures in the critical evaluation

In order to evaluate a number of original works critically, the following items have been referred to from the original papers, using the properly designed "Extraction Form":

The investigators

The laboratory where the research was carried out

The nature of the journal in which the work was published

The method of the experimental measurements

Calibration of the apparatus

Correction of the experimental results

Considerations and precautions paid on the measuring techniques

The experimental errors reported

The fundamental constants used

The overall accuracy estimated by the original authors

Purity of the sample used.

Furthermore, the original data have been plotted in a large graph, and the scattering of the experimental

data has been also considered in the present evaluation. When the old values of fundamental constants were used in the original report, the final values have been recalculated as mentioned in the preceding section, if necessary.

The final evaluation has been performed by the Committee members and several researchers in this field of Japan, referring to the extraction forms mentioned above, as well as the interpolated values at the common temperatures and pressures. The weight in this critical evaluation has been given to each original work. Then, the weighted mean value has been taken as the most probable value at each point of common temperatures and pressures. The standard deviation has been also calculated at the data point.

Evaluation of Compressibility Factors of Methane

The references on the P - V - T relations of methane were searched for and collected by the HPDCJ. A list of literature on these properties was published as the Reference List Series No. 4 in 1971. Although there exist 87 references on the P - V - T relations of methane, only nine papers are available on the original experimental data as listed below:

- F. G. Keyes and H. G. Burks (1927)¹¹⁾
- H. M. Kvalnes and V. L. Gaddy (1931)¹²⁾
- A. Michels and G. W. Nederbragt (1936)¹³⁾
- R. H. Olds, H. H. Reamer, B. H. Sage and W. N. Lacey (1943)¹⁴⁾
- H. W. Schamp, Jr., E. A. Mason, A. C. B. Richardson and A. Altman (1958)¹⁵⁾
- H. Iwasaki and K. Date (1961)¹⁶⁾
- D. R. Douslin, R. H. Harrison, R. T. Moore and J. T. McCullough (1964)¹⁷⁾
- L. Deffet and F. Ficks (1965)¹⁸⁾
- S. L. Robertson and S. E. Babb, Jr. (1969)¹⁹⁾

The original data of P - V - T relations of methane have been first extracted from these papers listed above. The compressibility factors have been calculated and, if necessary, small corrections have been made based on the temperature scale and fundamental constants, as described in the preceding sections. Then, the values at specified common temperatures and pressures have been computed by the method of interpolation mentioned above. These sets of data have been carefully examined in details and critically evaluated. From the view point of the experimental procedures and precautions, three sets of

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- 11) F. G. Keyes and H. G. Burks, *J. Am. Chem. Soc.*, **49**, 1403 (1927)
 - 12) H. M. Kvalnes and V. L. Gaddy, *ibid.*, **55**, 394 (1931)
 - 13) A. Michels and G. W. Nederbragt, *Physica*, **2**, 1000 (1935); **3**, 549 (1936)
 - 14) R. H. Olds, H. H. Reamer, B. H. Sage and W. N. Lacey, *Ind. Eng. Chem.*, **35**, 922 (1943)
 - 15) H. W. Schamp, Jr., E. A. Mason, A. C. B. Richardson and A. Altman, *Phys. Fluids*, **1**, 329 (1958)
 - 16) H. Iwasaki and K. Date, *Chem. Resear. Instit. Non-Aqueous Solutions*, **10**, 67 (1961)
 - 17) D. R. Douslin, R. H. Harrison, R. T. Moore and J. T. McCullough, *J. Chem. Eng. Data*, **9**, 358 (1964)
 - 18) L. Deffet and F. Ficks, "Advances in Thermophysical Properties at Extreme Temperatures and Pressures", p. 107, ASME, New York (1965)
 - 19) S. L. Robertson and S. E. Babb, Jr., *J. Chem. Phys.*, **51**, 1357 (1969)

Evaluation of *P-V-T* Relations

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Table 1 The most probable values of compressibility factor of methane

Pressure (atm)	Temperature (°C)									
	0°	25°	50°	75°	100°	125°	150°	175°	200°	225°
20	**0.95216 (0.00013)	0.96525 (0.00010)	0.97467 (0.00011)				**0.99400 (0.00000)			
30	0.92859 (0.00018)	0.94846 (0.00013)	0.96257 (0.00012)	0.97292 (0.00012)	0.98061 (0.00010)	0.98669 (0.00006)	0.99135 (0.00003)	**0.99493 (0.00008)	**0.99744 (0.00008)	**1.00034 (0.00001)
40	0.90514 (0.00031)	0.93206 (0.00015)	0.95109 (0.00014)	0.96476 (0.00014)	0.97499 (0.00010)	0.98290 (0.00008)	0.98899 (0.00004)	**0.99377 (0.00010)	**0.99732 (0.00010)	**1.00087 (0.00004)
50	0.88210 (0.00025)	0.91620 (0.00016)	0.94007 (0.00017)	0.95710 (0.00014)	0.96977 (0.00011)	0.97947 (0.00010)	0.98696 (0.00006)	**0.99285 (0.00011)	**0.99744 (0.00010)	**1.00161 (0.00001)
60	0.85950 (0.00023)	0.90101 (0.00017)	0.92969 (0.00013)	0.94997 (0.00013)	0.96498 (0.00013)	0.97644 (0.00011)	0.98526 (0.00007)	**0.99218 (0.00012)	**0.99744 (0.00012)	**1.00161 (0.00001)
70	0.83798 (0.00020)	0.88650 (0.00024)	0.91986 (0.00012)	0.94355 (0.00022)	0.96065 (0.00017)	0.97381 (0.00010)	0.98388 (0.00007)	**0.99177 (0.00013)	**0.99782 (0.00013)	**1.00258 (0.00001)
80	0.81776 (0.00026)	0.87308 (0.00029)	0.91080 (0.00015)	0.93760 (0.00026)	0.95681 (0.00020)	0.97159 (0.00013)	0.98286 (0.00010)	**0.99167 (0.00020)	**0.99843 (0.00017)	**1.00371 (0.00013)
90	0.79920 (0.00039)	0.86088 (0.00019)	0.90259 (0.00018)	0.93210 (0.00010)	0.95348 (0.00023)	0.96977 (0.00013)	0.98215 (0.00010)	**0.99181 (0.00021)	**0.99927 (0.00018)	**1.00510 (0.00018)
100	0.78267 (0.00056)	0.84999 (0.00016)	0.89529 (0.00022)	0.92748 (0.00013)	0.95065 (0.00025)	0.96839 (0.00016)	0.98174 (0.00013)	**0.99227 (0.00028)	**1.00033 (0.00019)	**1.00664 (0.00017)
120	0.75693 (0.00083)	0.83236 (0.00024)	0.88361 (0.00022)	0.92011 (0.00012)	0.94666 (0.00023)	0.96687 (0.00016)	0.98212 (0.00013)	**0.99398 (0.00034)	**1.00320 (0.00028)	**1.01040 (0.00025)
140	**0.74244 (0.00091)	0.82069 (0.00014)	0.87602 (0.00033)	0.91392 (0.00010)	0.94490 (0.00019)	0.96706 (0.00013)	0.98379 (0.00013)	**0.99679 (0.00031)	**1.00694 (0.00031)	**1.01494 (0.00031)
160	**0.73870 (0.00061)	**0.81600 (0.00033)	0.87280 (0.00027)	0.91469 (0.00013)	0.94547 (0.00015)	0.96904 (0.00013)	0.98686 (0.00018)	**1.00086 (0.00047)	**1.01167 (0.00045)	**1.02021 (0.00031)
180	**0.74544 (0.00058)		0.87403 (0.00015)	0.91603 (0.00030)	0.94827 (0.00013)	0.97264 (0.00011)	0.99123 (0.00025)	**1.00580 (0.00044)	**1.01716 (0.00044)	**1.02634 (0.00048)
200	**0.75968 (0.00084)		0.87913 (0.00014)	0.92106 (0.00023)	0.95323 (0.00015)	0.97799 (0.00018)	0.99702 (0.00019)	**1.01200 (0.00034)	**1.02366 (0.00046)	**1.03300 (0.00036)
250			0.90743 (0.00057)	0.94395 (0.00041)	0.97406 (0.00006)	0.99814 (0.00018)	1.01661 (0.00018)	**1.03171 (0.00014)	**1.04348 (0.00028)	**1.05285 (0.00035)
300			0.95080 (0.00016)	**0.98016 (0.00030)	**0.98016 (0.00030)	**1.02663 (0.00016)	1.04329 (0.00017)	**1.05690 (0.00001)	**1.06780 (0.00012)	**1.07648 (0.00019)
350			**1.00319 (0.00106)	**1.02483 (0.00059)	**1.02483 (0.00059)	**1.06146 (0.00038)	1.07535 (0.00027)	**1.08683 (0.00037)	**1.09593 (0.00008)	**1.10357 (0.00006)
400			**1.06167 (0.00152)			1.08893 (0.00063)	**1.11094 (0.00004)			
450			**1.12380 (0.00159)			1.13781 (0.00085)				
500			**1.18894 (0.00130)			**1.18854 (0.00082)				
550			**1.25612 (0.00141)			**1.24217 (0.00098)				
600			**1.32151 (0.00126)			**1.29571 (0.00091)				

(): Value of standard deviation
 ** : Determined from two original data
 ***: Determined from three original data

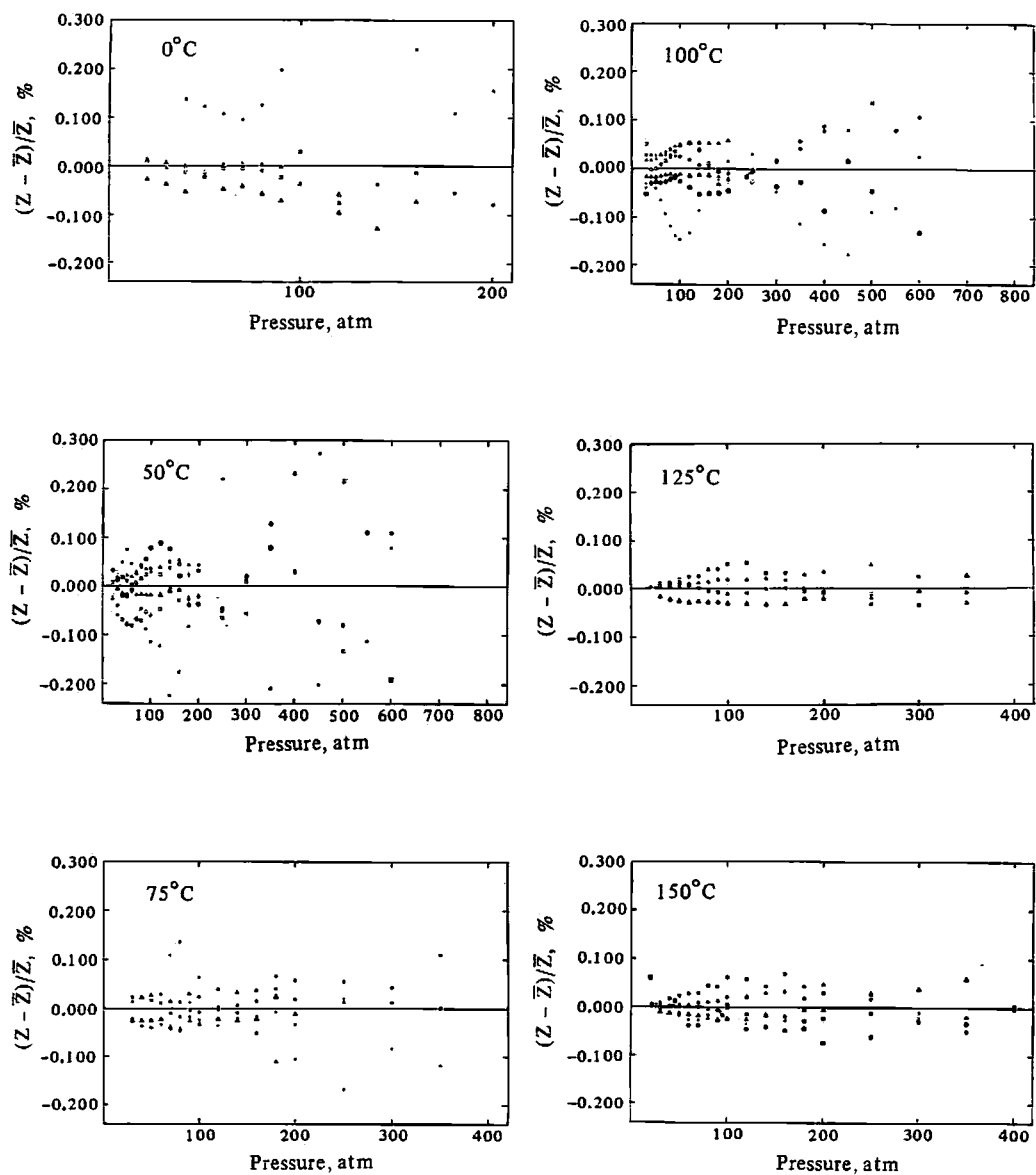


Fig. 1 Percentage deviation diagrams

▲: Ref 13), ×: Ref 16), ○: Ref 14)
 □: Ref 17), △: Ref 15), ●: Ref 18)

data¹³⁾¹⁵⁾¹⁷⁾ are considered to be the most reliable and the highest weight has been given to them. Weight second to the above has been given to three other sets of data¹⁴⁾¹⁶⁾¹⁸⁾ in the present analysis. No weight has been given to two earlier works¹¹⁾¹²⁾, nor to the recent paper¹⁹⁾ in which the data were reported in higher pressure range than the present common pressures.

The most reliable values of the compressibility factors of methane have been determined by taking the weighted mean at every common temperature and pressure. The final recommended values are shown in Table 1 with the standard deviations. The percentage deviations of the original data from the tabulated values have been calculated by:

$$\text{percentage deviation} = \frac{100(Z - \bar{Z})}{\bar{Z}} .$$

where Z is the compressibility factor interpolated from the original measurements, and \bar{Z} is the most probable values determined in this evaluation. Some of them are given graphically in Fig. 1.

Conclusion

The method of the critical evaluation of the P - V - T relation has thus been established and the most reliable values of the compressibility factors of gaseous methane are determined. This method will be applicable to other gases, and therefore, we have just initiated the work on the new evaluation of the compressibility factors of ethane and ethylene. Furthermore, since the present results can be used to produce the new equations of state, new efforts will be also concentrated on this field by the HPDCJ.