EVALUATION AND CORRELATION OF DIFFUSION COEFFICIENT DATA

The most Probable Values of the Self-Diffusion Coefficients of Gaseous Methane

BY SHINJI TAKAHASHI* AND HIROJI IWASAKI**

The experimental diffusion coefficient data of gaseous methane available in the literature have been evaluated from the view-point of their reliability, and correlated with temperature and pressure. The most probable values are presented in the table covering the range of temperature from 198.15 to 348.15 K and that of pressure up to 260×10^5 Pa.

Introduction

The present work is one of the program of High Pressure Data Center of Japan organized in the Society of Materials Science, Japan, under the sponsorship of the Agency of Science and Technology. The following members attended the meetings for the discussion concerning this work: J. Osugi, Y. Takezaki (Kyoto Univ.); T. Makita, Y. Tanaka (Kobe Univ.); I. Tanishita (Ikutoku Tech. Univ.); K. Watanabe, A. Nagashima (Keio Univ.); K. Date (Tohoku Univ.), to whom the authors wish to express sincere gratitude for their valuable suggestions and discussions.

Survey of Diffusion Coefficient Data

There exist six reports[1~6] on the measurement of the self-diffusion coefficient of gaseous methane under high pressure. The first author's names, the methods of measurement, the temperature range, and the maximum pressures are listed in Table 1. The original papers were examined and evaluated from the view-point of the reliability of the reported data by the Committee members as described above. It was concluded that the difference in the reliability of the various methods could not be found at the present time, but the data obtained by Jeffries *et al.*[1] were very different from those obained by

(*Received, April 21, 1976*)

* Department of Chemical Engineering, Tohoku University, Sendai

** Chemical Research Institute for Non-Aqueous Solutions, Tohoku University, Sendai

1) Q. R. Jeffries and H. G. Drickamer, *J. Chem. Phys.*, **21**, 1358 (1953)
2) N. J. Trappeniers and P. H. Oosting, *Phys. Lett.*, **23**, 445 (1966)
3) D. E. Woesner, B. S. Snowdon, Jr., R. A. George and J. C. Melrose, *IEC Fundamentals*, **8**, 779 (1969)
4) A. T. Hu and R. Kobayashi, *J. Chem. Eng. Data*, **15**, 328 (1970)
5) R. Dawson, F. Khoury and R. Kobayashi, *AIChE J.*, **16**, 725 (1970)
6) S. Takahashi, *Bull. Chem. Soc. Japan*, **45**, 2074 (1972)

Table 1 Measurements of the self-diffusion coefficient of gaseous methane

First Author	Year	Method	Temp. Range (K)	Max. Press. (10^5 Pa)	Ref. No.
Jeffries	1953	Loschmidt type	273~323	304	1
Trappeniers	1966	Spin echo	190~308	235	2
Woesner	1969	Spin echo	298~364	173	3
Hu	1970	Gas chromathography	298	62	4
Dawson	1970	Spin echo	298~354	414	5
Takahashi	1972	Two-chamber type	298~348	250	6

the other investigators. Therefore, no weight was given to the data obtained by Jeffries *et al.*, and equal weight was given to those obtained by the other five works.

Method and Results of Correlation

The values of temperature, pressure, density, and diffusion coefficient in the papers were reduced to SI units as follows:

temperature, T, in K
pressure, P, in 10^5 Pa ($=1$ bar$=0.9869$ atm)
density, ρ, in g/cm^3
diffusion coefficient, D, in cm^2/s.

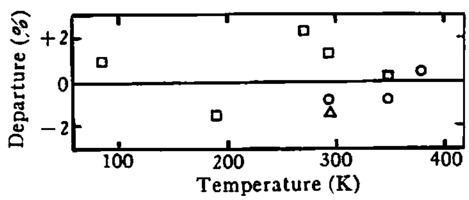

Fig. 1 Percentage departure of the experimental values from Eq. (1)
△: 10), □: 11), ○: 12)

The method of correlation is the grid-point method, which was employed in the previous work[7] carried out in the program of High Pressure Data Center of Japan. Generally the diffusion coefficients of gases (D) are approximately inversely proportional to pressure (P) or density (ρ), and accurate interpolation of D-values to grid-points is not easy in the D *vs.* P or the D *vs.* ρ curves. However, the change of the product, DP or $D\rho$ with pressure or density is not so large as that of D itself. Therefore, the quantities, DP or $D\rho$, were correlated to temperature and to pressure or density in the present work.

First, the correlation of DP to P was tried, but the DP *vs.* P isotherms were curved very steeply

7) T. Makita, Y. Tanaka and A. Nagashima, This Journal, **43**, 54 (1973)

Table 2 The mean grid-point values of $D\rho$ for gaseaus methane in $10^{-6}\,gs^{-1}\,cm^{-1}$

ρ ($10^{-3}\,g\,cm^{-3}$) \ T (K)	198.15	223.15	248.15	273.15	298.15	323.15	348.15
	103[a]	117[a]	131[a]	144[a]	155[a]	165[a]	174[a]
10	104	115	126	136	151	161	172
20	104	116	127	137	152	161	172
30	105	117	128	138	152	163	172
40	105	117	128	139	153	163	172
50	106	117	128	139	155	164	172
60	106	118	129	139	155	164	173
70	106	118	129	140	155	165	172
80	107	118	129	140	156	166	168
90	104 [b]	118	129	140	156	166	167
100	104	118	129	140	151	160	172
110	104	118	129	140	151	160	172
120	104	118	129	140	155	166	172
130	104	118	128	139	155	166	172
140	104	119	131	141	155	165	171
150	104	118	128	138	154	166	171
160	104	118	127	138	154	166	158
180		117	123	132	141	150	155
200		115	120	129	138	147	152
220		112	119	126			
240		108	115	122			
260		104	110				
280		100	106				
300		94	102				

a) The value at normal pressure calculated by Eq. (1).
b) The values enclosed by the dotted lines are single point values which were determined from only one set of experimental data available in the literature.

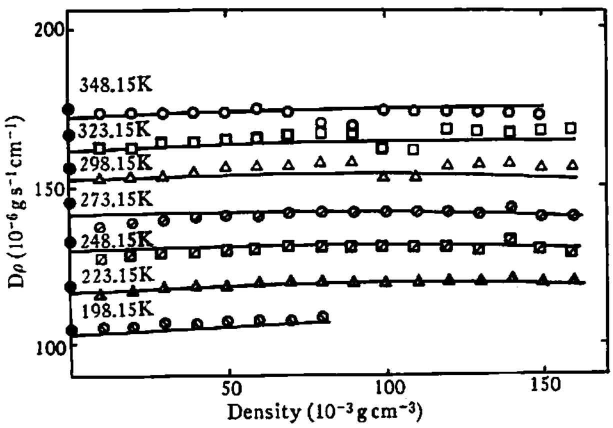

Fig. 2 The mean grid-point values and their smoothed values of $D\rho$ for gaseous methane
○, □, △, ⊘, ⊠, ▲, ⦸: the mean grid-point value,
●: the value at normal pressure
—: the smoothed value

The Review of Physical Chemistry of Japan Vol. 46 No. 2 (1976)

Table 3 The smoothed grid-point values of $D\rho$ for gaseous methane in $10^{-6}\,gs^{-1}\,cm^{-1}$

ρ ($10^{-3}\,g\,cm^{-3}$) \ T (K)	198.15	223.15	248.15	273.15	298.15	323.15	348.15
	103[a]	116[a]	129[a]	141[a]	152[a]	162[a]	172[a]
10	104	116	129	141	152	163	173
20	104	116	129	141	152	163	174
30	105	116	129	141	152	163	174
40	106	117	129	141	152	163	175
50	106	117	129	141	152	163	175
60	106	117	129	141	152	163	175
70	106	118	129	141	152	163	175
80	106	118	129	141	152	163	175
90		118	139	141	152	163	175
100		118	130	141	152	163	175
110		119	130	141	152	163	175
120		119	130	141	152	164	175
130		118	130	141	152	164	175
140		118	130	141	152	164	175
150		118	129	141	152	164	175
160		117	129	140	152	164	

a) The value at normal pressure.

below 273.15 K and some experimental points were distant from each other, and so there were the wide regions where interpolation was impossible. Therefore, the DP *vs.* P relation seemed to be unfavorable. Then, the quantity, $D\rho$, was correlated to temperature and to density. In order to reduce the reported values to the $D\rho$ *vs.* ρ relation, the density-values were estimated from the equation of state obtained by Tanishita *et al.*[8] above 273.15 K, and from the one obtained by Vennix *et al.*[9] below 273.15 K*, because the experimental conditions were specified by temperature and pressure in most cases. In the measurement of Trappeniers *et al.*[2], however, temperature and density were used to specify the conditions; then, the density values given by them were adopted for the correlation of their data in the present work.

The $D\rho$-values at grid-points of temperature and pressure were obtained from the original data. When the reported data were not at grid-points, interpolation was carried out along the isotherms and the isochores by using the method of least squares. In this procedure precaution was paid for the interpolated values to keep up the experimental accuracy in each original work. The mean values at grid-points were calculated with equal weight.

8) I. Tanishita, K. Watanabe, H. Kondo and A. Nakashima, *This Journal* **42**, 125 (1973)

9) A. J. Vennix and R. Kobayashi, *AIChE J.*, **15**, 926 (1969)

* The equation of state obtained by Tanishita *et al.* is valid only above 273.15 K, and so the one obtained by Vennix *et al.* was used below 273.15 K. It was confirmed that the average difference of compressibility factors calculated by the two equations is 0.08%, and the maximum is 0.13% at 273.15 K in the pressure range up to 168×10^5 Pa.

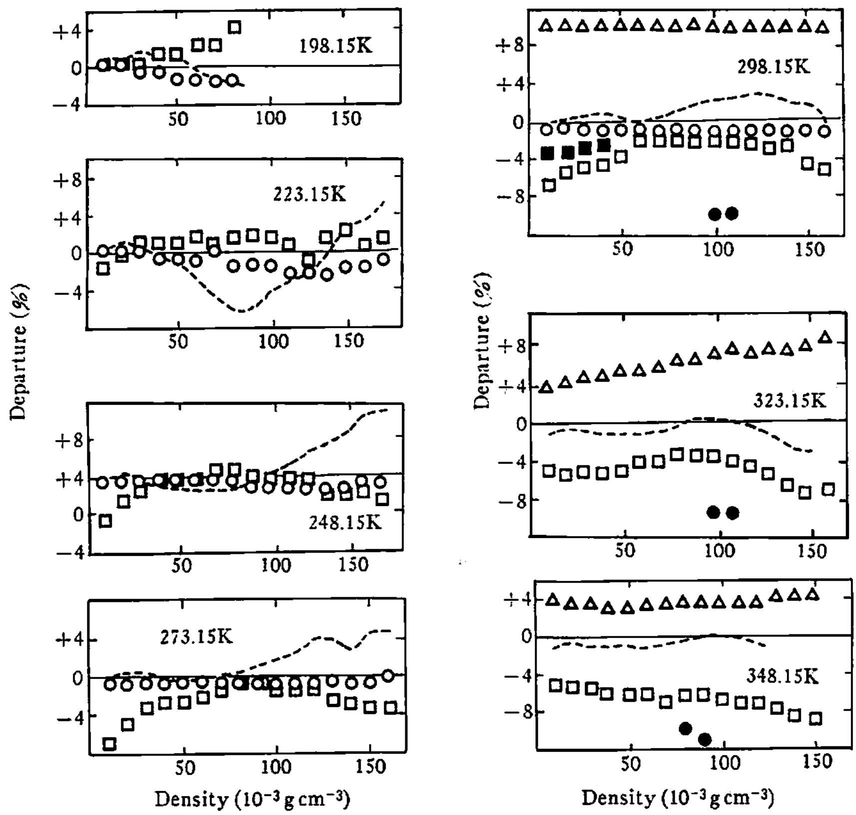

Fig. 3 Percentage departure of the original $D\rho$-values from the smoothed ones
○: 2), □: 5), △: 6), ●: 3), ■: 4), ⋯: 14)

On the other hand, three sets of experimental data[10~12] at normal pressure are available for gaseous methane. They were fitted to the following cubic equation as a function of temperature:*

$$D=0.0540-0.9159\times10^{-3}T+0.7456\times10^{-5}T^2-0.7794\times10^{-8}T^3 \quad (1)$$

Eq. (1) was found to fit the experimental data in the range from 90.2 to 382.6 K with the average deviation of 1.0% and the maximum of 2.6%. The departures of the original data from the above equation are plotted in Fig. 1.

It may be noted that the theoretical equation, (2)

10) E. B. Winn and E. P. Ney, *Phys. Rev.*, **72**, 77 (1947)
11) E. B. Winn, *Phys. Rev.*, **80**, 1024 (1950)
12) C. R. Mueller and R. W. Cahill, *J. Chem. Phys.*, **40**, 651 (1964)

* Conventional equation representing the relation of the diffusion coefficients of gases at normal pressure with temperature is $D=D_0(T/T_0)^m$, where T_0 is 273.15 K and D_0 is the diffusion coefficient at T_0 K. When the diffusion coefficient data for methane were fitted to this equation, $D_0=0.198$ and m=1.8296 were obtained. The average deviation of the calculated values by this equation from the experimental ones was 2.3%, and the maximum was 7.3%.

Table 4 The most probable values of the self-diffusion coefficient of gaseous methane in $10^{-3}cm^2s^{-1}$

P (10^5 Pa) \ T(K)	198.15	223.15	248.15	273.15	298.15	323.15	348.15
1.013	103	133	164	197	232	268	307
5	20.7	26.2	32.6	39.6	46.6	54.3	61.9
10	9.97	12.8	16.0	19.6	23.1	27.0	30.9
20	4.74	6.07	7.75	9.51	11.4	13.3	15.3
30	2.77	3.82	4.98	6.18	7.43	8.77	10.2
40	1.82	2.71	3.59	4.52	5.48	6.50	7.58
50		2.03	2.75	3.53	4.31	5.14	6.01
60		1.55	2.21	2.86	3.53	4.23	5.00
70		1.20	1.81	2.40	2.98	3.59	4.26
80		0.966	1.53	2.05	2.57	3.11	3.70
90		0.791	1.30	1.78	2.25	2.74	3.27
100			1.13	1.57	2.00	2.45	2.93
110			0.991	1.40	1.80	2.21	2.65
120			0.890	1.26	1.63	2.01	2.42
130			0.810	1.15	1.49	1.85	2.23
140				1.06	1.38	1.71	2.07
150				0.983	1.28	1.59	1.93
160				0.920	1.20	1.49	1.81
170					1.13	1.41	1.70
180					1.07	1.33	1.61
190					1.02	1.27	1.53
200					0.969	1.21	1.45
220						1.11	1.33
240						1.03	1.23
260							1.15

$$D=0.0026280\frac{\sqrt{T^3/M}}{P\sigma^2\Omega^{(1,1)*}} \tag{2}$$

presented by Hirschfelder *et al.*[13] reproduces the experimental data with the average deviation of 2.6 % and with the maximum of 9.1% (90.2 K) in the range from 90.2 to 382.6 K by using the following parameters for the Lennard-Jones (12-6) potential: $\varepsilon/k=151$ K, $\sigma=3.664$ Å. The parameters were determined for Eq. (2) to fit the experimental diffusion coefficient data by using the method of least suqares.

The mean values, $D\rho$, the single point values, and the values of $D\rho$ at normal pressure calculated by Eq. (1) are shown in Table 2. In the procedure every tabulated value under high pressure was determined independently of the adjacent values and the smoothness among these values has not been found to be satisfactory. Therefore, the $D\rho$-values in Table 2 were smoothed, first, by using the linear

13) J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, "Molecular Theory of Gases and Liquids", John Wiley & Sons Inc., New York (1954), p. 539

equations of temperature at each constant density, and then, by using the cubic equations of density including the $D\rho$-values at normal pressure at each constant temperature. The smoothed values thus obtained are shown in Table 3 and Fig. 2 along with the mean grid-point values. The average difference of the mean grid-point values from the smoothed ones was 1.1%, and the maximum was 4.6%.

Percentage departures of the original $D\rho$-values from the smoothed ones are shown in Fig. 3, where departure (%)$=100\times\{(D\rho)_i-(D\rho)_{sm}\}/(D\rho)_{sm}$, $(D\rho)_i$=the original values at the grid-point, $(D\rho)_{sm}$=the smoothed grid-point values. For comparison the departures of the values calculated from the chart presented by Takahashi[14] are shown with dashed lines.

In Table 4 the D-values calculated from Table 3 are shown against pressure at each constant temperature.

14) S. Takahashi, *J. Chem. Eng. Japan*, **7**, 417 (1974)