BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(6), 1342—1345 (1974)

The Diffusion of Gases at High Pressures. V. The Diffusion of CTH_3 in the CO_2–Ar System

Shinji Takahashi

Chemical Research Institute of Non-aqueous Solutions, Tohoku University, Katahira, Sendai 980

(Received October 5, 1973)

The diffusion coefficients of radioactive methane (CTH_3) in argon and in mixtures of carbon dioxide with argon(0.719, 0.497, and 0.245 mol fractions of argon) were measured at the temperatures of 25, 50, and 75 °C in the 15∼250 atm pressure range. The measurements were made through a plug of porous bronze in the diffusion cell by using the radioactive tracer technique. The diffusion coefficient-density products, $D\rho$, for the CTH_3-argon system increased slightly with the density in the region below 5 mol/l, and decreased slightly in the region above 5 mol/l. The $D\rho$ for the CTH_3-mixture systems decreased slightly with the density over the whole range studied here. The density dependence of $D\rho$-values at high densities could not be predicted by Enskog-Thorne's theory.

This investigation is a part of a continuing research project into the diffusion coefficients of gases at high pressures. The previous investigations were made for the diffusion coefficients of $^{14}CO_2$ in the CO_2–Ar[1,2] and CO_2–CH_4 system[3] and for those of CTH_3 in the CH_4–CO_2 system.[4] This paper will present the diffusion coefficients of CTH_3 in the CO_2–Ar system. Measurements were made at the temperatures of 25, 50, and 75 °C in the 15∼250 atm pressure range. The mole fractions of argon in the mixtures were 0.719, 0.497, and 0.245.

Experimental

The apparatus and the experimental procedure were the same as those described previously.[1] The diffusion path in the cell was porous bronze plug with pores of about 10 μ. Radioactive methane (CTH_3), obtained from the New England Nuclear Corp., was diluted with non-radioactive methane to a specific activity of about 450 μCi/mmol. The purities of the carbon dioxide and argon used in this investigation were 99.9%. Mixtures of carbon dioxide with argon were prepared in the cylinders. The exact compositions were determined by absorbing carbon dioxide from samples into a potassium hydroxide solution. Under the conditions studied, the mixtures were not in a liquid state.[5]

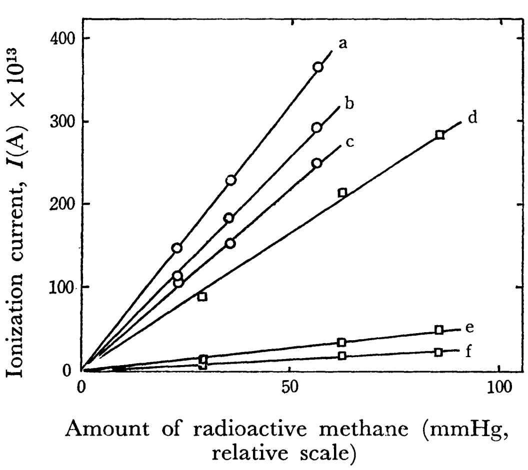

Fig. 1. Relations between the amounts of radioactive methane and the ionization currents at 50 °C.
○: for pure argon, □: for the mixture of 0.497 mol fraction of argon. Pressure(atm) — a, d: 14.55; b, e: 97.8; c: 243.0; f: 194.6

The proportionality between the concentration of radioactive methane and the ionization current, essential for a quantitative treatment of the diffusion data, was confirmed experimentally for pure argon and for mixtures. As examples, the results for pure argon and for the mixture of the 0.497 mol fraction of argon at 50 °C are shown in Fig. 1.

Results and Discussion

In Table 1, showing the experimental results, D is the diffusion coefficients of radioactive methane (CTH_3) in argon and in mixtures. The densities of argon were calculated from the compressibility factors obtained by Michels *et al.*[6] The densities of carbon dioxide–argon mixtures were calculated by using the compressibility chart described in a previous paper.[2] In Fig. 2 the diffusion coefficient-density products, $D\rho$, are plotted against the densities. Curves a, b, c, and d are drawn through the experimental points for the systems where the mole fractions of argon, x_3, are 1.000, 0.719, 0.497, and 0.245. Curve e has been obtained in a previous investigation[4] for the diffusion of CTH_3 with carbon dioxide; it is shown for the sake of comparison. The D at $x_3=1.000$ is the diffusion coefficient of radioactive methane with argon, D_{13}, where the subscripts 1 and 3 denote radioactive methane and argon respectively. The values of $D_{13}\rho$ increase slightly with the density in the region below 5 mol/l, and decrease slightly in the region above 5 mol/l.

The extrapolation of $D\rho$ *vs.* ρ curves to 1 atm provides a basis for comparison with published low-pressure experimental results and with theoretical values. Applying the mass correction[7] to the binary diffusion coefficient of normal methane with argon, D_{43}, which was measured by Carswell[8] at only 25 °C, the binary diffusion coefficient of radioactive methane with argon, D_{13}, was obtained. On the other hand, theoretical values of D_{13} at 1 atm were obtained by applying the mass correction to the binary diffusion coefficients of normal methane with argon, D_{43}, given by:[9]

$$(D_{43})^\circ = 0.002628\frac{\sqrt{T^3(M_4+M_3)/2M_4M_3}}{p\sigma_{43}{}^2\Omega_{43}{}^{(1,1)*}}$$

Here, $(D_{43})^\circ$ is the first approximation to diffusion coefficient of normal methane with argon (cm^2/s); T, the temperature (K); M, the molecular weight;

TABLE 1. EXPERIMENTAL RESULTS

P atm	ρ $mol \cdot l^{-1}$	$D \times 10^3$ $cm^2 \cdot s^{-1}$	$D\rho \times 10^3$ $cm^2 \cdot mol \cdot s^{-1} \cdot l^{-1}$
		25 °C	
		$x_3 = 1.000$	
14.45	0.5953	15.8	9.41
14.47	0.5961	15.2	9.06
14.58	0.6007	14.9	8.95
48.9	2.0534	4.53	9.30
49.7	2.0876	4.51	9.42
50.9	2.1393	4.44	9.50
101.5	4.3480	2.23	9.70
109.0	4.6791	2.05	9.60
144.3	6.2262	1.49	9.28
196.4	8.4359	1.12	9.45
245.6	10.3753	0.885	9.18
		$x_3 = 0.719$	
14.37	0.5990	14.24	8.53
14.41	0.6007	13.7	8.23
49.9	2.1781	3.83	8.34
50.9	2.2159	3.94	8.73
100.0	4.6435	1.82	8.45
147.1	7.1057	1.16	8.24
184.6	9.0550	0.934	8.46
219.8	10.7418	0.721	7.74
		$x_3 = 0.497$	
14.32	0.6074	12.3	7.47
14.41	0.6113	13.0	7.95
50.3	2.3394	3.34	7.81
50.4	2.3444	3.29	7.71
101.0	5.3565	1.41	7.55
101.5	5.3900	1.49	8.03
149.2	8.6154	0.904	7.38
202.5	12.1441	0.601	7.48
		$x_3 = 0.245$	
14.37	0.6198	11.2	6.94
14.40	0.6212	11.3	7.02
50.0	2.5426	2.79	7.09
68.6	3.7330	1.89	7.06
82.3	5.2595	1.43	7.52
84.3	5.4868	1.24	6.80
99.9	7.5693	0.914	6.92
122.4	10.9569	0.650	6.84
		50 °C	
		$x_3 = 1.000$	
14.41	0.5462	17.1	9.34
14.41	0.5462	17.1	9.34
14.41	0.5462	17.0	9.26
14.44	0.5473	17.1	9.36
50.1	1.9209	4.91	9.43
50.9	1.9655	4.71	9.26
99.2	3.8405	2.54	9.75
101.8	3.9325	2.48	9.78
149.8	5.8045	1.61	9.35
200.4	7.6976	1.21	9.31
201.8	7.7481	1.19	9.22
235.8	8.9572	1.08	9.67
253.5	9.5604	0.974	9.31
		$x_3 = 0.719$	
50.1	1.9821	4.40	8.72
50.3	1.9903	4.42	8.80
101.2	4.1708	2.11	8.80
151.2	6.3936	1.31	8.38
200.9	8.5362	0.982	8.38
		$x_3 = 0.497$	
14.37	0.5556	14.2	7.89
14.50	0.5606	13.8	7.75
49.8	2.0423	3.83	7.82
99.3	4.4457	1.68	7.47
148.6	7.0861	1.09	7.72
247.0	12.0139	0.593	7.12
		$x_3 = 0.245$	
13.82	0.5416	13.8	7.47
14.41	0.5657	12.8	7.24
50.2	2.2125	3.32	7.35
100.5	5.4049	1.32	7.13
148.2	9.2849	0.727	6.75
		75 °C	
		$x_3 = 1.000$	
14.41	0.5057	19.6	9.91
14.41	0.5057	19.7	9.96
50.0	1.7654	5.76	10.17
101.8	3.6060	2.66	9.59
151.0	5.3286	1.88	10.02
202.6	7.0695	1.33	9.40
247.1	8.4947	1.17	9.94
		$x_3 = 0.719$	
14.37	0.5082	18.5	9.40
14.39	0.5089	18.1	9.21
50.4	1.8284	4.86	8.89
50.9	1.8480	4.90	9.06
51.4	1.8662	4.98	9.29
97.8	3.6454	2.46	8.97
122.6	4.6160	1.92	8.86
152.5	5.7884	1.54	8.91
201.7	7.6493	1.13	8.64
250.0	9.3874	0.890	8.35
		$x_3 = 0.497$	
14.41	0.5133	16.5	8.47
14.41	0.5133	16.7	8.57
14.41	0.5133	17.0	8.73
50.4	1.8772	4.56	8.56
50.6	1.8848	4.52	8.52
101.0	4.0034	2.12	8.49
101.8	4.0392	2.08	8.40
149.6	6.1655	1.39	8.50
197.8	8.3520	0.965	8.06
		$x_3 = 0.245$	
14.37	0.5187	15.6	8.09
14.31	0.5165	15.2	7.85
51.0	2.0052	3.96	7.94
96.8	4.2627	1.83	7.80
126.3	5.9224	1.32	7.82
150.3	7.3604	0.991	7.29
193.0	9.8887	0.746	7.38

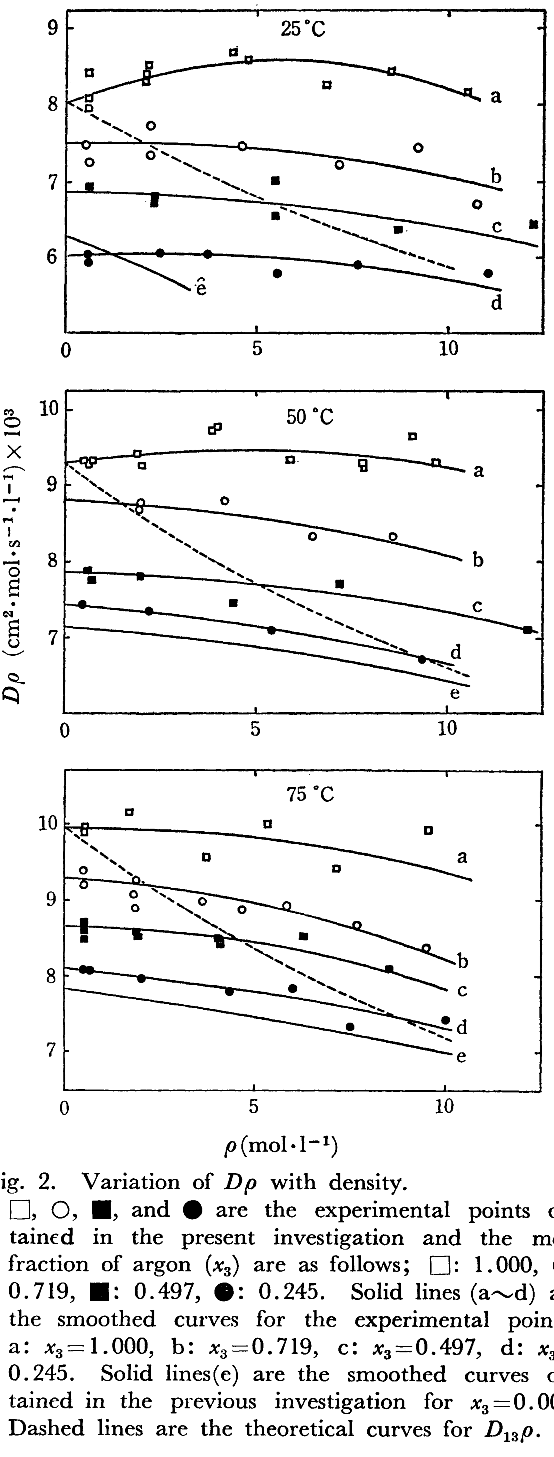

Fig. 2. Variation of $D\rho$ with density.
□, ○, ■, and ● are the experimental points obtained in the present investigation and the mole fraction of argon (x_3) are as follows; □: 1.000, ○: 0.719, ■: 0.497, ●: 0.245. Solid lines (a~d) are the smoothed curves for the experimental points; a: $x_3=1.000$, b: $x_3=0.719$, c: $x_3=0.497$, d: $x_3=0.245$. Solid lines(e) are the smoothed curves obtained in the previous investigation for $x_3=0.000$. Dashed lines are the theoretical curves for $D_{13}\rho$.

p, the pressure (atm); σ_{43}, the potential parameter (Å); $\Omega_{43}^{(1,1)*}$, the reduced collision integral. The subscripts 3 and 4 denote argon and normal methane respectively. The values obtained by Carswell and the theoretical values are compared with those extrapolated in this investigation in Table 2. The deviation of the value obtained by Carswell from that extrapolated is not small, but the deviation of the theoretical values are −5~−10%, consistent with those of the values observed for other systems.[10]

According to Enskog-Thorne's theory,[11] which is the only theoretical treatment offering any practical application, the binary diffusion coefficient at high pressures is given by:

$$D_{13}\rho = (D_{13})^{\circ}\rho/\chi_{13} \tag{2}$$

Here, $(D_{13})^{\circ}$ is the binary diffusion coefficient calculated on the basis of the low-density kinetic theory; it is obtained by applying the mass correction to the values given, for example, by Eq. (1). χ_{13} is a correction factor depending on the density of gas; it is given by:

$$\chi_{13} = 1 + 0.2618 n_1\sigma_1^3(8-3\sigma_1/\sigma_{13}) + 0.2618 n_3\sigma_3^3(8-3\sigma_3/\sigma_{13}) + \cdots\cdots \tag{3}$$

where n_1 and n_3 are the numbers of molecules per unit volume (cm⁻³) and where σ_1 and σ_3 are the collision diameters (cm). σ_{13} is $(\sigma_1+\sigma_3)/2$ according to an empirical combining rule. Since radioactive methane is present as only a trace in this investigation, the second term on the right-hand side of Eq. (3) may be neglected. In the calculation of $D_{13}\rho$ at high pressures by means of Eqs. (2) and (3), the extrapolated values of $D_{13}\rho$ at 1 atm were used in place of $(D_{13})^{\circ}\rho$; σ_1 and σ_3 are approximated by the parameters for the Lennard-Jones (12-6) model—3.882 Å for normal methane and 3.418 Å for argon.[12] As is shown in Fig. 2, the theoretical values of $D_{13}\rho$ decrease with the density; they are about 26% lower than those obtained in the present experiment at $\rho=5$ mol/l. Such discrepancies, which have been found for many systems,[13] seem to result from the fact that, in the derivation of Eq. (3), the rigid-sphere model was assumed and the properties of real gases were not taken into consideration. Therefore, it may be expected that the agreement between the theory and the experiment will be better if χ_{13} is evaluated from the P-V-T relations of real gases according to Enskog's suggestion. The results obtained by applying his suggestion will be reported later.

Table 2. Comparison of the extrapolated values (D_{extra}) of the binary diffusion coefficients at 1 atm with the theoretical values (D_{theor}) and with that reported by Carswell (D_{obs})

CTH_3-Ar system

Temp. °C	D_{extra} cm²·s⁻¹	D_{theor} cm²·s⁻¹	D_{obs} cm²·s⁻¹	Dev.[a] %
25	0.220		0.194	−11.8
25		0.198		−10.0
50	0.247	0.229		−7.3
75	0.277	0.263		−5.1

a) Dev. (%) = $(D_{\text{theor}}-D_{\text{extra}})\times 100/D_{\text{extra}}$
or $(D_{\text{obs}}-D_{\text{extra}})\times 100/D_{\text{extra}}$

The diffusion coefficients of radioactive methane in mixtures, D_{1m}, at 1 atm may be calculated by using Wilke's equation:[14]

$$1/D_{1m} = x_2/D_{12} + x_3/D_{13} \tag{4}$$

Here, x_2 and x_3 are the mole fractions of carbon dioxide and argon, D_{12} and D_{13} are the binary diffusion coefficients of radioactive methane with carbon dioxide and with argon, and $x_2+x_3 \doteqdot 1$. In Table 3 the values of D_{1m} at 1 atm given by Eq. (4) are compared with

Table 3. Comparison of the extrapolated values of the diffusion coefficients of the trace-component (CTH_3) in the mixtures ($D_{1m,extra}$) with those calculated using Wilke's equation($D_{1m,calc}$)

Temp. °C	CTH_3(trace)-(CO_2+Ar) system $D_{1m,extra}$ $cm^2\cdot s^{-1}$	$D_{1m,calc}$ $cm^2\cdot s^{-1}$	Dev.[a] %
	x_3(mole fraction of argon) = 0.719		
25	0.205	0.210	+2.7
50	0.234	0.228	−2.6
75	0.266	0.259	−2.6
	x_3 = 0.497		
25	0.193	0.199	−3.1
50	0.209	0.214	+2.4
75	0.248	0.246	−0.8
	x_3 = 0.245		
25	0.173	0.188	+8.7
50	0.196	0.200	+2.0
75	0.232	0.233	+0.4
		average[b]	2.8

a) Dev. (%) = $(D_{1m,calc}-D_{1m,extra})\times 100/D_{1m,extra}$. b) average of the absolute values of Dev.

those extrapolated. In the calculation of D_{1m} at 1 atm by using Eq. (4), the values extrapolated in this investigation were used for D_{12} and those extrapolated in the previous paper[4] were used for D_{13}. As is shown in Table 3, the deviation is 2.8% on the average; therefore, Eq. (4) seems to be approximately valid.

As Enskog-Thorne's theory has not yet been extended to ternary systems, the prediction of $D_{1m}\rho$ at high pressures was made by using Eq. (5), derived from Eq. (4):

$$1/D_{1m}\rho = x_2/D_{12}\rho + x_3/D_{13}\rho \qquad (5)$$

where D_{1m}, D_{12}, and D_{13} are the values at the same density, ρ(mol/l), and where $x_2+x_3 \fallingdotseq 1$. According to Eq. (5) $D_{1m}=D_{12}$ at $x_3=0$, $D_{1m}=D_{13}$ at $x_3=1$, and $1/D_{1m}\rho$ should vary linearly with x_3. By using the values of $D_{1m}\rho$ read from the smoothed curves in Fig. 2, the values of $1/D_{1m}\rho$ were plotted against the mole fractions of argon, x_3, at ρ=2, 4, 6, 8, and 10 mol/l in Fig. 3. Although the plots do not give very good straight lines, the deviation of the values given by Eq. (5) from the smoothed values obtained in Fig. 2 is 2.1% on the average; therefore, Eq. (5) seems to be approximately valid also at high pressures in the present system.

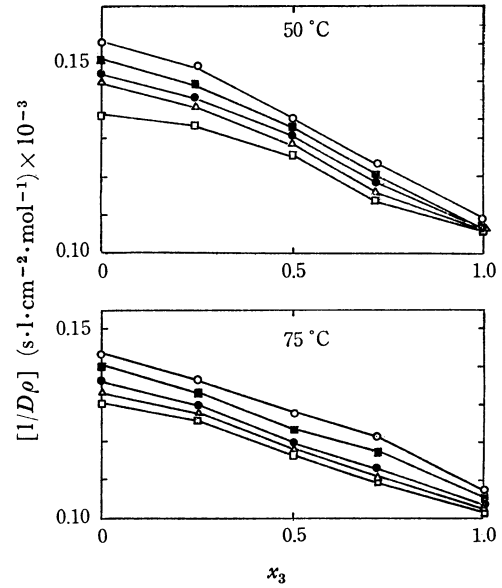

Fig. 3. Variation of $1/D\rho$ with composition. Density ($mol\cdot l^{-1}$); □: 2, △: 4, ●: 6, ■: 8, ○: 10

The author wishes to express his deep gratitude to Professor Hiroji Iwasaki for his kind direction and encouragement throughout this work.

References

1) S. Takahashi and H. Iwasaki, This Bulletin, **39**, 2105 (1966).
2) S. Takahashi, This Bulletin, **41**, 1573 (1968).
3) S. Takahashi and H. Iwasaki, *Rev. Phys. Chem. Japan*, **38**, 28 (1968).
4) S. Takahashi, This Bulletin, **45**, 2074 (1972).
5) G. Kaminishi, Y. Arai, S. Saito, and S. Maeda, *J. Chem. Eng. Japan*, **1**, 109 (1968).
6) A. Michels, Hub. Wijker, and H.K. Wijker, *Physica*, **15**, 2074 (1949).
7) F. Hutchinson, *J. Chem. Phys.*, **17**, 1081 (1949).
8) A. T. Carswell and J. C. Stryland, *Can. J. Phys.*, **41**, 708 (1963).
9) 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.
10) R. C. Reid and T. K. Sherwood, "The Properties of Gases and Liquids," McGraw-Hill Book Company, Inc., New York (1958), p. 274.
11) S. Chapman and T. G. Cowling, "The Mathematical Theory of Non-uniform Gases," Cambridge Univ. Press, London (1960), p. 292.
12) Ref. 9, p. 1110.
13) For example, L. Durbin and R. Kobayashi, *J. Chem. Phys.*, **37**, 1643 (1962).
14) C. R. Wilke, *Chem. Eng. Progress*, **46**, 95 (1950).