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The Diffusion of Gases at High Pressures. II. The Diffusion of $^{14}CO_2$ in the $^{12}CO_2$-Ar System

Shinji TAKAHASHI

Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Katahira-cho, Sendai

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The diffusion coefficients of $^{14}CO_2$ in argon and in binary mixtures of normal carbon dioxide and 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 using the radioactive tracer technique. The products of the binary diffusion coefficient of $^{14}CO_2$ in argon and the density increase with an increase in the density. This tendency is not predicted by Enskog-Thorne's mixed dense gas theory, which requires that the products decrease with an increase in the density. The products of the diffusion coefficient of $^{14}CO_2$ in the mixtures and the density increase slightly with an increase in the density in the region of lower density at each temperature. However, in the region of higher density they decrease slightly at 25 and 50°C and are nearly constant at 75°C. The values extrapolated to 1 atm agree fairly well with the experimental findings of Holsen *et al.* and those predicted by kinetic theory.

Kinetic theory precicts[1,2] that, at low pressures, the effective diffusion coefficient, D, of a trace component, i, in a gas mixture will be given by the equation:

$$1/D = \sum_{j \neq i} x_j/D_{ij} \tag{1}$$

where x_j is the mole fractions and D_{ij}, the binary diffusion coefficients. This equation has been confirmed by several recent experimental investigations.[3] At high pressures, however, much less is known about the diffusion in a multicomponent system either theoretically or experimentally. Recently, though, a few studies of high-pressure diffusion with ternary systems, $^{14}CO_2$-$^{12}CO_2$-CH_4,[4] $^{14}CO_2$-$^{12}CO_2$-H_2,[5] and $^{14}CO_2$-$^{12}CO_2$-C_3H_8,[5] have been made.

In the present paper the diffusion coefficients of $^{14}CO_2$ in argon and in binary mixtures of normal carbon dioxide and argon at the temperatures of 25, 50, and 75°C in the 15—250 atm pressure range are reported on.

Experimental

The experimental apparatus and procedure have been described in detail in a previous paper.[6] Exactly the same procedure was followed. In the present investigation a type-II porous plug with a grain size of ϕ 60—70 μ was used; the apparatus constant, K_{II}, determined at 25°C is shown in Table 1. K_{II}'s at 50 and 75°C were determined in the previous paper.[6] The proportionality between the ionization current and the concentration of $^{14}CO_2$, essential for the quantitative treatment of diffusion data, was confirmed experimentally for pure argon and for each mixture at a constant temperature and pressure. For example, the results at 50°C are shown in Figs. 1 and 2.

TABLE 1. DETERMINATION OF APPARATUS CONSTANT, K_{II} AT 25°C

P atm	$K_{II}D_{22}P\times10^6$ * atm/sec	$D_{22}\times10^3$ ** cm²/sec	$K_{II}\times10^3$ 1/cm²
10	826	11.2	7.38
20	783	5.30	7.39
30	732	3.26	7.48
40	669	2.25	7.43
50	587	1.62	7.25
		Average	7.39

* The smoothed values of $K_{II}D_{22}P$ obtained experimentally.

** The self-diffusion coefficients of normal carbon dioxide obtained in the previous paper.[6]

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[3] D. F. Fairbanks and C. R. Wilke, *Ind. Eng. Chem.*, **42**, 471 (1950); H. Wise, *J. Chem. Phys.*, **31**, 1414 (1959); R. E. Walker, N. De Haas and A. A. Westenberg, *ibid.*, **32**, 1314 (1960); B. N. Srivastava and R. Paul, *Physica*, **28**, 646 (1962); L. Miller and P. C. Carman, *Trans. Faraday Soc.*, **57**, 2143 (1961); **60**, 33 (1964); T. A. Pakurar and J. R. Ferron, *Ind. Eng. Chem. Fundamentals*, **5**, 553 (1966); A. Saran and Y. Singh, *Can. J. Chem.*, **44**, 2222 (1966); H. Watts, *Trans. Faraday Soc.*, **60**, 1745 (1964); *Can. J. Chem.*, **43**, 431 (1965); **45**, 1825 (1967).

[4] Q. R. Jeffries and H. G. Drickamer, *J. Chem. Phys.*, **22**, 436 (1954).

[5] C. Chou and J. J. Martin, *Ind. Eng. Chem.*, **49**, 758 (1957).

[6] S. Takahashi and H. Iwasaki, This Bulletin, **39**, 2105 (1966).

TABLE 2. EXPERIMENTAL RESULTS

P atm	ρ mol/l	$D\times10^3$ cm^2/sec	$D\rho\times10^3$ cm$^2\cdot$mol/sec$\cdot l$
25°C			
x_3 (mole fraction of argon)$=1.000$			
10.57	0.4343	14.1	6.12
20.6	0.8515	7.46	6.35
20.8	0.8602	7.35	6.32
20.9	0.8647	7.24	6.26
30.9	1.286	4.95	6.37
40.7	1.702	3.76	6.40
51.6	2.170	2.97	6.44
60.8	2.569	2.48	6.37
97.6	4.178	1.56	6.52
151.6	6.543	1.01	6.61
204.8	8.780	0.793	6.96
249.8	10.53	0.666	7.01
$x_3=0.719$			
14.61	0.6096	9.40	5.73
20.4	0.8607	6.54	5.63
60.3	2.679	2.17	5.81
102.6	4.777	1.26	6.02
151.6	7.341	0.804	5.90
200.4	9.837	0.621	6.11
201.5	9.893	0.601	5.95
247.5	11.90	0.495	5.89
$x_3=0.497$			
14.48	0.6130	8.77	5.38
20.3	0.8717	6.09	5.31
61.9	2.966	1.84	5.46
90.9	4.710	1.14	5.37
102.7	5.467	1.00	5.47
146.3	8.467	0.650	5.50
150.1	8.733	0.626	5.47
199.7	11.98	0.447	5.36
$x_3=0.245$			
20.7	0.9150	5.48	5.01
30.9	1.440	3.54	5.10
31.3	1.457	3.43	5.10
51.1	2.606	1.91	4.98
51.2	2.616	1.97	5.15
70.2	4.050	1.24	5.02
101.0	7.724	0.652	5.04
120.1	10.62	0.447	4.75
148.4	13.99	0.334	4.67
50°C			
$x_3=1.000$			
14.50	0.5520	11.7	6.46
14.96	0.5671	11.6	6.58
15.35	0.5820	11.2	6.52
64.2	2.470	2.69	6.64
69.0	2.658	2.47	6.57
102.2	3.958	1.68	6.65
114.1	4.470	1.50	6.71
147.6	5.721	1.21	6.92
151.9	5.885	1.15	6.77
171.4	6.623	1.03	6.82
209.5	8.028	0.869	6.98
220.7	8.429	0.834	7.03
249.8	9.444	0.741	7.00
$x_3=0.719$			
14.51	0.5550	10.7	5.94
15.02	0.5746	10.5	6.03
15.31	0.5859	10.1	5.92
51.3	2.032	3.00	6.10
52.2	2.069	2.95	6.10
52.7	2.089	2.91	6.08
75.6	3.056	2.00	6.11
86.6	3.531	1.75	6.18
96.2	3.952	1.56	6.17
101.2	4.171	1.47	6.13
103.2	4.259	1.45	6.18
110.2	4.570	1.34	6.12
135.7	5.705	1.10	6.28
150.4	6.361	0.963	6.13
200.4	8.516	0.710	6.05
205.5	8.724	0.685	5.98
248.5	10.41	0.583	6.07
252.9	10.57	0.566	5.98
$x_3=0.497$			
14.44	0.5583	9.88	5.52
14.44	0.5583	9.80	5.47
14.45	0.5588	9.81	5.48
54.4	2.254	2.51	5.66
103.8	4.678	1.24	5.80
104.2	4.699	1.22	5.73
151.3	7.235	0.789	5.71
200.5	9.846	0.584	5.75
245.5	11.95	0.475	5.68
$x_3=0.245$			
14.36	0.5641	9.09	5.13
14.39	0.5650	9.03	5.10
14.49	0.5690	9.17	5.22
51.4	2.274	2.37	5.39
54.6	2.445	2.20	5.38
105.9	5.811	0.933	5.42
150.3	9.475	0.567	5.37
191.4	12.56	0.424	5.33
75°C			
$x_3=1.000$			
13.99	0.4910	13.9	6.82
50.6	1.787	3.90	6.97
50.9	1.797	3.94	7.08
98.5	3.489	2.04	7.12
104.5	3.701	1.92	7.11
157.6	5.555	1.28	7.11
202.5	7.066	1.03	7.28

Table 2 (Continued)

P atm	ρ mol/l	$D\times10^3$ cm^2/sec	$D\rho\times10^3$ cm^2·mol/sec·l
239.4	8.252	0.872	7.20
	$x_3=0.719$		
13.83	0.4890	13.0	6.36
45.4	1.642	3.88	6.37
52.9	1.923	3.40	6.54
112.5	4.220	1.53	6.46
151.1	5.733	1.16	6.65
196.5	7.470	0.878	6.56
247.1	9.286	0.701	6.51
	$x_3=0.497$		
14.44	0.5140	11.7	6.01
52.1	1.945	3.14	6.11
52.1	1.945	3.16	6.15
101.0	3.981	1.57	6.25
153.3	6.341	0.980	6.21
200.4	8.467	0.738	6.25
	$x_3=0.245$		
14.42	0.5206	11.0	5.73
14.43	0.5210	11.0	5.73
51.3	2.019	2.90	5.85
51.6	2.031	2.92	5.93
101.5	4.517	1.31	5.92
156.2	7.713	0.771	5.95

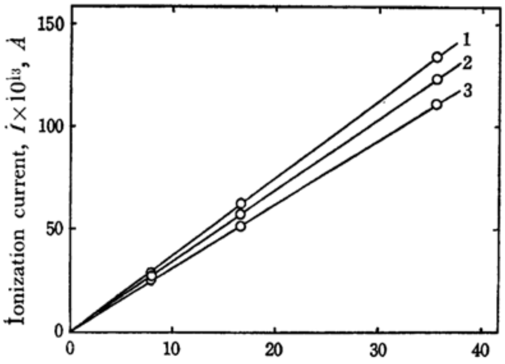

Fig. 1. Relations between the amount of $^{14}CO_2$ and ionization current in argon at 50°C.
1: 15 atm 2: 100 atm 3: 250 atm

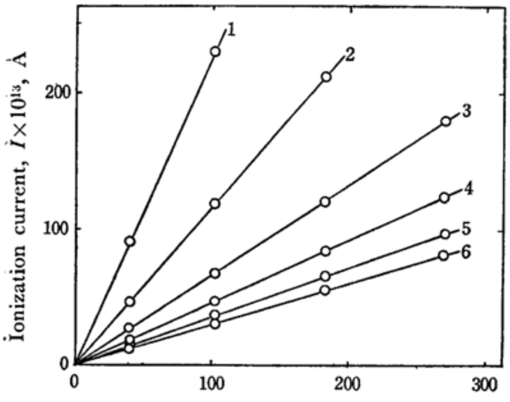

Fig. 2. Relations between the amount of $^{14}CO_2$ and ionization current in the mixture of $x_3=0.497$ at 50°C.
1: 15 atm 2: 50 atm 3: 100 atm
4: 150 atm 5: 200 atm 6: 250 atm

The nonradioactive mixtures were prepared from carbon dioxide and argon, certified to be 99.9 and 99.99% pure, respectively. Except for drying with silica gel, no further purification was attempted. Before measuring the diffusion, bulk mixtures of normal carbon dioxide-argon were prepared in storage cylinders. Their exact compositions were determined by bubbling samples through a potassium hydroxide solution. For this investigation the mixtures are not in the liquid state.[7]

Results and Discussion

The experimental results are given in Table 2. The densities, ρ (mol/l), for argon were calculated from the compressibility factors obtained by Michels *et al.*[8] The densities for carbon dioxide-argon mixtures were calculated by using the compressibility chart*1 with the pseudo critical temperature, T_c, and pressure, P_c, obtained by the following relations:

$$T_c = x_2(T_c)_2 + x_3(T_c)_3 \tag{2}$$

$$P_c = x_2(P_c)_2 + x_3(P_c)_3 \tag{3}$$

where the subscripts 2 and 3 denote normal carbon dioxide and argon. The compressibility calculated above agrees within 2.1% with Abraham's data,[10] which range from 50 to 1000 atm at 50°C. It may be noted that the maximum deviation of the values calculated from Abraham's data by using Weber's chart is 4.6%.

In Fig. 3 the diffusion coefficient-density products, $D\rho$, are plotted against the densities.

The values of $D\rho$ at a unit mole fraction of argon

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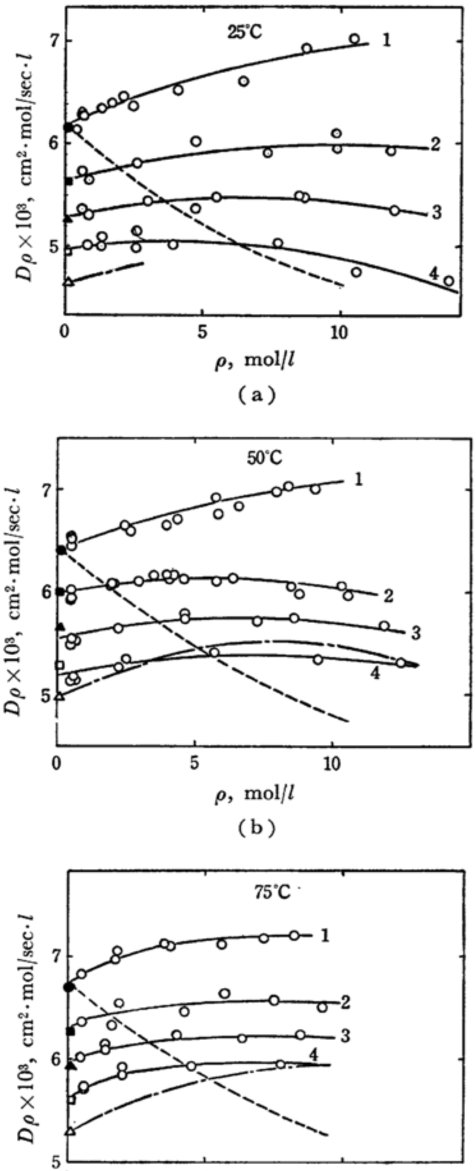
[7] G. Kaminishi, Private communication.

[8] A. Michels, Hub. Wijker and HK Wijker, *Physica*, **15**, 627 (1949).

*1 This chart was prepared from the compressibility data with carbon dioxide and argon using the same method as was used for Weber's generalized compressibility chart.[9]

[9] H. C. Weber, "Thermodynamics for Chemical Engineers," John Wiley & Sons, Inc., New York (1939).

[10] W. H. Abraham and C. O. Bennett, *A. I. Ch. E. Journal*, **6**, 257 (1960).



(a)

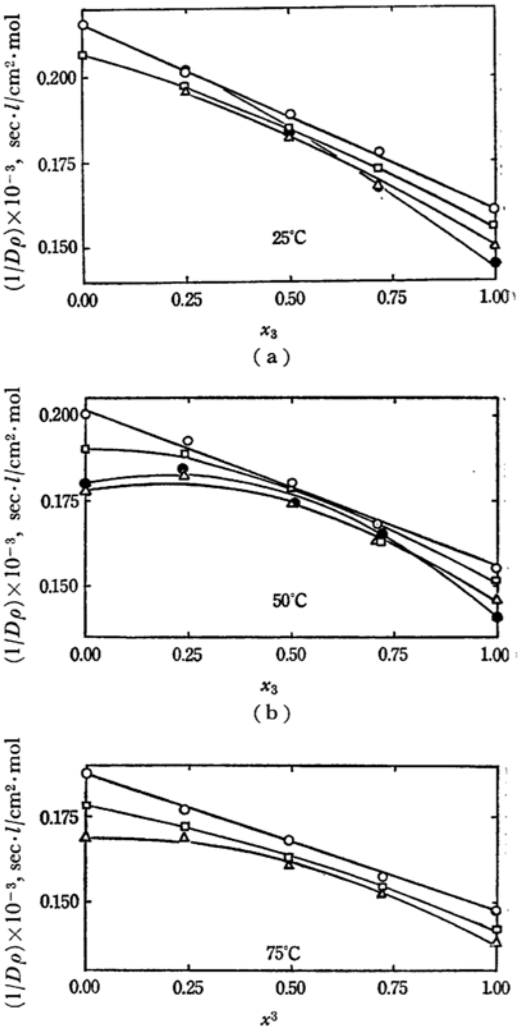
(b)

(c)

Fig. 3. Experimental results.
○: Present work, ——: Smoothed curves for experimental values, 1: $x_3=1.000$, 2: $x_3=0.719$, 3: $x_3=0.497$, 4: $x_3=0.245$. —·—: Smoothed curves for $D_{12}\rho$ obtained in the previous paper.⁶⁾ ----: Theoretical curves. ●: Calculated at 1 atm by the formula of Holsen for D_{13}. ■, ▲ and □: Calculated at 1 atm by using Eq. (6) for the mixtures of $x_3=0.719$, 0.497 and 0.245, respectively. △: Calculated at 1 atm from the experimental values for D_{12}.¹⁴⁾

are equivalent to the binary diffusion coefficients of the $^{14}CO_2$-Ar system. These products at each temperature show a tendency to increase consistently with an increase in the density. The extrapolation of these products to 1 atm provides a basis for comparison with the low-pressure experimental results reported by other investigators. The formula of the experimental binary diffusion coefficients for the carbon dioxide-argon system published by Holsen *et al.*¹¹⁾ yields values which are in agreement with the extrapolated values of this investigation.

The effect of the density (or the pressure) on the binary diffusion coefficient may be predicted by Enskog-Thorne's mixed dense gas theory,¹²⁾ which



(a)

(b)

(c)

Fig. 4. Relations between $(1/D\rho)$ and x_3.
○: 1 atm, □, △ and ●: 2, 6 and 10 mol/l, respectively.

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11) J. N. Holsen and M. R. Strunk, *Ind. Eng. Chem. Fundamentals*, **3**, 143 (1964).

12) S. Chapman and T. G. Cowling, "The Mathematical Theory of Non-Uniform Gases," Cambridge University Press, London (1960).

is the only theoretical treatment offering any practical application. It is expressed as follows:

$$D_{13}\rho = (D_{13})^\circ \rho / \chi_{13} \qquad (4)$$

$$\chi_{13} = 1 + 0.2618 n_3 \sigma_3{}^3 (8 - 3\sigma_3/\sigma_{13}) \qquad (5)$$

where the subscript 1 denotes radioactive carbon dioxide. D_{13} is the first approximation to the diffusion coefficient for dense gases, and $(D_{13})^\circ$ is the first approximation to the diffusion coefficient for dilute gases. The n is the number of molecules per unit of volume, and σ is the effective collision diameter. The empirical combining law, $\sigma_{13} = (\sigma_1 + \sigma_3)/2 \fallingdotseq (\sigma_2 + \sigma_3)/2$, was employed in the calculation. The collision diameters, $\sigma_2 = 3.996$ Å and $\sigma_3 = 3.418$ Å, were taken from Ref. 1 and are those determined from the viscosity measurements for the Lennard-Jones model. $(D_{13})^\circ$ was calculated by using the formula published by Holsen *et al.*,[11] with a mass correction. As is shown in Fig. 3 by dashed lines, the theory requires the $D_{13}\rho$ products to decrease with an increase in the density. The calculated products are lower by 28% at a density of about 8 moles per liter at each temperature. This poor agreement is in accordance with most of the other high-pressure-diffusion results.[13]

According to Eq. (1), the effective diffusion coefficient, D, of a trace component (radioactive carbon dioxide) in a gas mixture of normal carbon dioxide and argon is given by the equation:

$$1/D = x_2/D_{12} + x_3/D_{13} \qquad (6)$$

where D_{12} and D_{13} are the binary diffusion coefficients of radioactive carbon dioxide in normal carbon dioxide and in argon respectively. The values of D_{12} and D_{13} at 1 atm were obtained by applying the mass corrections to the reported values of the self-diffusion coefficient of normal carbon dioxide, D_{22}[14], and to that of the binary diffusion coefficient between normal carbon dioxide and argon, D_{23}.[11] The calculated values of $D\rho$ at 1 atm thus obtained for intermediate concentrations are shown in Fig. 3. These calculated values are in agreement with the extrapolated values.

The Enskog theory has not yet been extended to ternary systems at high pressures. Therefore, the applicability of Eq. (1) to the high-pressure-diffusion coefficient was tested in the form:

$$1/D\rho = x_2/D_{12}\rho + x_3/D_{13}\rho \qquad (7)$$

$$x_2 + x_3 \fallingdotseq 1$$

where D, D_{12}, and D_{13} are the values at density, ρ. Equation (7) indicates that $1/D\rho$ may vary linearly with either x_2 or x_3, that $D = D_{12}$ at $x_2 = 1$, and that $D = D_{13}$ at $x_3 = 1$. The values of $D\rho$ were read from the smoothed curves in Fig. 3, while the values of $1/D\rho$ are plotted against the mole fraction of argon, x_3, at 1 atm and $\rho = 2$, 6, and 10 mol/l in Fig. 4. The plots are straight lines at 1 atm. However, they are not straight lines but convex curves at densities above 2 moles per liter.

Conclusion

At high pressures the binary diffusion coefficient of $^{14}CO_2$ in argon can not be predicted by Enskog-Thorne's theory, and the effect of the composition on the diffusion coefficient of $^{14}CO_2$ in $^{12}CO_2$-Ar mixtures does not follow Eq. (1). These facts are understandable, for the above-mentioned theory has been derived for rigid spherical molecules, while Eq. (1) is only for ideal gases.

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

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13) E. W. Becker, W. Vogell and F. Zigan, *Z. Naturforschg.*, **8a**, 686 (1953); H. A. O'Hern, Jr., and J. J. Martin, *Ind. Eng. Chem.*, **47**, 2081 (1955); V. J. Berry, Jr., and R. C. Koeller, *A. I. Ch. E. Journal*, **6**, 274(1960); L. Durbin and R. Kobayashi, *J. Chem. Phys.*, **37**, 1643 (1962).

14) I. Amdur, J. W. Irvine, Jr., E. A. Mason and J. Ross, *J. Chem. Phys.*, **20**, 436 (1952).