THE DIFFUSION COEFFICIENTS OF $^{14}\text{CO}_2$ IN THE $\text{CO}_2\text{-N}_2$ SYSTEM AT HIGH PRESSURE

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The diffusion coefficients of radioactive carbon dioxide ($^{14}\text{CO}_2$) in nitrogen and in mixtures of carbon dioxide with nitrogen were measured at temperatures of 25, 50, and 75°C and at pressures ranging from 15 to 250 atm with an error of 3%. Mole fractions of nitrogen in the mixtures were 0.741, 0.515, and 0.238. The measurements were made through a plug of porous bronze in a diffusion cell of two-chamber type by using radioactive tracer technique. The diffusion coefficient-density products decreased slightly with increasing density or remained nearly constant. The diffusion coefficients at high pressure obtained in this study agreed fairly well with those calculated from the generalized chart, which was prepared from the correlation of the experimental data. The binary diffusion coefficients of a trace of radioactive carbon dioxide in nitrogen at high pressure could be predicted by a modified Enskog-Thorne's theory.

Introduction

This study is a part of the continuing research project to measure the diffusion coefficients of gases at high pressure. The previous studies were made for the diffusion coefficients of $^{14}\text{CO}_2$ in the $\text{CO}_2\text{-Ar}$ system^{15,16)} and $\text{CO}_2\text{-CH}_4$ system¹⁷⁾; for those of CTH_3 in the $\text{CO}_2\text{-CH}_4$ system¹⁸⁾ and $\text{CO}_2\text{-Ar}$ system¹⁹⁾. This paper presents the diffusion coefficients of $^{14}\text{CO}_2$ in the $\text{CO}_2\text{-N}_2$ system. Measurements were made at temperatures of 25, 50, and 75°C and at pressures ranging from 15 to 250 atm. Mole fractions of nitrogen in mixtures were 0.741, 0.515, and 0.238.

1. Experimental

The apparatus and the experimental procedure were the same as those described previously¹⁵⁾. The diffusion path in the cell was a plug of porous bronze with pores of about 10 μ in diameter. The temperature of the diffusion cell was measured by use of a thermistor thermometer calibrated with a standard mercury thermometer and kept constant within 0.1°C. The error in temperature measurement was within 0.05°C. The pressure was measured by use of Bourdon gauges calibrated with a pressure balance of free-piston type. The errors in pressure measurement were within 0.02 atm up to 20 atm, 0.1 atm for pressures ranging from 20 to 50 atm, and 0.5 atm for pressures ranging from 50 to 250 atm. Radioactive carbon dioxide ($^{14}\text{CO}_2$) was generated by adding a 60 wt. % aqueous solution of HClO_4 to $\text{Ba}^{14}\text{CO}_3$; its specific radioactivity was approximately 450 $\mu\text{Ci}/\text{mmol}$; that is, the mole

fraction of $^{14}\text{CO}_2$ in this gas was about 0.0071. Addition of this gas to the nitrogen or to the mixtures in the cell by about 0.5 vol. % enabled us to obtain the ionization current, 90×10^{-13} amp, required for the determination of the diffusion coefficient. The purities of the normal carbon dioxide and nitrogen used were 99.9 and 99.999 %, respectively. The mixtures of carbon dioxide with nitrogen were prepared in cylinders. Their exact compositions were determined by absorbing carbon dioxide from samples into a 2-normal aqueous solution of potassium hydroxide. The error in composition determination was within 0.2 %. Under the conditions studied, the mixtures are not in a liquid state⁹⁾.

2. Results

The experimental results are given in Table 1 and Fig. 1. The error in diffusion-coefficient determination was estimated to be within 3 % by taking into account the accuracy of ionization-current measurement. The scattering of the obtained values of diffusion coefficient was 1.3 % on the average and 3.4 % at maximum for the 13 experimental conditions; two runs were carried out for 1 condition, as shown in Table 1. The densities of gases, ρ , were calculated from the compressibility data given by Lunbeck *et al.*¹⁰⁾ for nitrogen, and by Haney *et al.*⁵⁾ for the carbon dioxide-nitrogen mixtures. The error in density determination was estimated to be within 0.1 % by taking into account the error of reported data and the uncertainty of interpolation. Figure 1 shows that the diffusion coefficient-density products, $D\rho$, slightly decrease almost linearly with increasing density, or remain nearly constant.

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Table 1 Experimental results

P [atm]	$\rho \times 10^3$ [mol/cm ³]	$D \times 10^3$ [cm ² /sec]	P [atm]	$\rho \times 10^3$ [mol/cm ³]	$D \times 10^3$ [cm ² /sec]
[25°C] $x_3=1.000$					
14.41	0.5898	12.1	14.35	0.5534	10.6*
50.7	2.0796	3.36	14.36	0.5536	11.1*
88.2	3.6000	1.98	51.6	2.1043	2.64
152.1	6.0599	1.12	102.4	4.4472	1.22
200.4	7.7433	0.887	151.3	6.8502	0.785
249.2	9.2713	0.720	209.7	9.5091	0.567
$x_3=0.741$			$x_3=0.515$		
14.32	0.5953	10.6*	14.41	0.5631	9.02
14.36	0.5971	10.3*	50.6	2.2367	2.20
50.5	2.1717	2.79*	74.3	3.6578	1.35
50.7	2.1802	2.80*	101.8	5.9518	0.853
103.0	4.5870	1.32	124.0	7.6921	0.695
153.3	6.8969	0.918	150.7	9.4857	0.536
202.5	8.9703	0.691			
244.5	10.536	0.581	[75°C] $x_3=1.000$		
$x_3=0.515$			14.36	0.5013	14.8*
14.37	0.6064	8.91*	14.36	0.5013	14.5*
14.38	0.6068	9.14*	50.5	1.7497	4.13*
50.5	2.3059	2.41*	50.5	1.7497	4.14*
51.0	2.3309	2.29*	102.9	3.5018	2.12
103.2	5.2564	1.02	152.0	5.0043	1.44
150.7	8.1422	0.665	202.5	6.8294	1.09
175.9	9.5886	0.557	245.7	7.7045	0.933
$x_3=0.238$			250.3	7.8240	0.951
14.41	0.6229	8.27*	$x_3=0.741$		
14.41	0.6229	7.92*	14.41	0.5079	13.2*
49.9	2.6132	1.91	14.41	0.5079	13.1*
78.9	**	0.925	50.2	1.7908	3.70
100.7	**	0.685	102.9	3.7056	1.82*
122.6	**	0.498	103.0	3.7092	1.70*
124.5	**	0.421	153.1	5.4886	1.17
147.5	**	0.373	200.5	7.0720	0.933
			247.0	8.5139	0.776
[50°C] $x_3=1.000$			$x_3=0.515$		
14.37	0.5415	13.6	14.24	0.5036	11.8*
50.5	1.8964	3.73	14.28	0.5079	11.8*
100.8	3.7321	1.93	50.4	1.8623	3.23*
154.3	5.5783	1.26	50.6	1.8695	3.17*
201.8	7.0859	0.975	103.4	3.9883	1.49
253.3	8.7769	0.831	148.7	5.8596	1.01
$x_3=0.741$			197.4	7.7068	0.747
14.41	0.5511	11.5	249.1	9.6980	0.575
50.6	1.9698	3.21	$x_3=0.238$		
103.8	4.1203	1.48	13.27	0.4778	11.8
151.5	6.0265	1.04	50.1	1.9590	2.88*
199.5	7.8284	0.803	50.4	1.9729	2.74*
250.1	9.5285	0.643	100.5	4.5334	1.24
			141.4	7.0791	0.793
			197.3	10.253	0.542

* These values were used to estimate the scattering of data.

** Reliable value could not be obtained.

3. Discussion

3.1 Chapman-Enskog's theory

The diffusion coefficient at $x_3=1.000$ is the mutual diffusion coefficient of radioactive carbon dioxide in nitrogen, D_{13} . The extrapolation of $D_{13}\rho$ vs. ρ curve to 1 atm provides a basis for comparison with published low-pressure experimental results and with theoretical values. By applying the mass correction⁷⁾ to the experimental values of D_{23} at 1 atm, which was measured by Walker *et al.*²²⁾, $D_{13,obs}$ was obtained. On the other hand, theoretical values, $D_{13,theor}$, at 1

○: $x_3=1.000$, □: $x_3=0.741$, △: $x_3=0.515$, ●: $x_3=0.238$

Fig. 1 Experimental results and comparison with theories

Table 2 Comparison of the values extrapolated to 1 atm, $D_{13,extra}$, with that observed by Walker *et al.*, $D_{13,obs}$, and the theoretical ones, $D_{13,theor}$

¹⁴ CO ₂ -N ₂ system				
t [°C]	$D_{13,extra}$ [cm ² /sec]	$D_{13,obs}$ [cm ² /sec]	$D_{13,theor}$ [cm ² /sec]	Dev.* [%]
25.0	0.172	0.167		-2.9
25.0	0.172		0.152	-11.6
50.0	0.194		0.176	-9.3
75.0	0.211		0.201	-5.6

* Dev. (%) = $(D_{13,obs} - D_{13,extra}) \times 100 / D_{13,extra}$
or $= (D_{13,theor} - D_{13,extra}) \times 100 / D_{13,extra}$

atm were obtained by applying the mass correction to $(D_{23})^0$, given by Eq. (1)⁶⁾.

$$(D_{23})^0 = 0.002628 \frac{\sqrt{T^3(M_2 + M_3)/2M_2M_3}}{P\sigma_{23}^2 Q_{23}^{(1,1)*}} \quad (1)$$

Here, $(D_{23})^0$ is the first approximation to D_{23} . In this calculation, $\sigma_{23} = (\sigma_2 + \sigma_3)/2$ and $\epsilon_{23} = (\epsilon_2 \cdot \epsilon_3)^{1/2}$ were assumed; $\sigma_2 = 3.996$ Å, $\sigma_3 = 3.681$ Å, $\epsilon_2/k = 190^\circ\text{K}$, and $\epsilon_3/k = 91.5^\circ\text{K}$ were used, which were determined by Johnston *et al.* for the Lennard-Jones 12-6 potential from the viscosity (Ref. 6, p. 1111). Table 2 shows the comparison of the values extrapolated to 1 atm in this study, $D_{13,extra}$, with $D_{13,obs}$ and $D_{13,theor}$. It can be seen from Table 2 that $D_{13,extra}$ agrees fairly well with $D_{13,obs}$. The deviations of $D_{13,theor}$ from $D_{13,extra}$ shown in Table 2 are similar to those of theoretical values given by Eq. (1) from experimental ones in various systems¹²⁾.

Table 3 The second and third virial coefficients of nitrogen

t [°C]	B_{SL} [cm ³ /mol]	B_{exp} [cm ³ /mol]	C_{SL} [cm ⁶ /mol ²]	C_{exp} [cm ⁶ /mol ²]
0	-10.13	-10.27	1339	1537
25	-4.48	-4.71	1215	1315
50	0.12	-0.28	1120	1219
75	3.92	3.20	1049	1257
100	7.10	6.56	990	1079
125	9.79	9.45	944	963
150	12.08	12.29	908	694

Fig. 2 Comparison of the values extrapolated to 1 atm with those calculated from Wilke's equation

3.2 Wilke's equation

The diffusion coefficient of a trace of radioactive carbon dioxide in the mixture at 1 atm, D_{1m} , is given by Wilke's equation, Eq. (2)²³⁾.

$$1/D_{1m} = x_2/D_{12} + x_3/D_{13} \quad (2)$$

Here, the value of D_{12} was taken from the data presented by Amdur *et al.*¹⁾; the value of D_{13} is that extrapolated to 1 atm for $x_3=1.000$ in the present study. **Figure 2** shows that Wilke's equation gives slightly higher values of D_{1m} than those extrapolated to 1 atm in this study. The deviation of the values of D_{1m} calculated by use of Eq. (2) from those extrapolated was about 4% on the average and the maximum was 6%.

3.3 Generalized chart

For predicting the diffusion coefficients of gases at high pressure the generalized charts may be used. At the present time those presented by Slattery *et al.*¹³⁾ and by the author²⁰⁾ are convenient for practical use. Hereafter, these are abbreviated to SB- and T-charts. The deviations of the values calculated by use of SB-chart from those observed were 7.2% on the average, and the maximum was 16.4%; those by use of T-chart were 2.0% on the average and the maximum was 7.4%.

3.4 Enskog-Thorne's theory

According to Enskog-Thorne's theory²⁾ the diffusion coefficient of a trace of radioactive carbon dioxide in nitrogen, D_{13} , at high pressure is given as follows:

$$D_{13}\rho/(D_{13}\rho)^0 = 1/\chi_{13} \quad (3)$$

$$\chi_{13} = 1 + (\pi/12)n_3(5 - 3\sigma_3/\sigma_{13})\sigma_3^3 + \dots \quad (4)$$

Here, $\sigma_{13} = (\sigma_1 + \sigma_3)/2$ and $\sigma_1 \doteq \sigma_2$ were assumed; the values of σ_2 and σ_3 were the same as those used in the

calculation of Eq. (1). The values predicted by use of Eqs. (3) and (4) are shown in Fig. 1 with the dotted lines. The deviations from observed values increase with increasing density and are about 30% at $\rho = 10 \times 10^{-3}$ mol/cm³.

Several investigators attempted to use the experimental PVT relations in order to obtain χ_{13} as follows^{3,11,21)}. From the equation of state, proposed by Enskog for a simple gas,

$$P + a_0\rho^2 = (RT/V)(1 + b_0\rho\chi) \quad (5)$$

$$\text{where } b_0 = (2/3)\pi N\sigma^3 \quad (6)$$

Equation (7) is obtained, by assuming that b_0 is independent of temperature (Ref. 2, p. 288).

$$b_0\rho\chi = (V/R)(\partial P/\partial T)_V - 1 \quad (7)$$

and Eq. (8) follows from Eq. (7) (Ref. 6, p. 560).

$$b_0 = B + T(dB/dT) \quad (8)$$

From Eqs. (7) and (8), χ can be determined by use of the experimental values of $(\partial P/\partial T)_V$ and B . Since the diffusion component is a trace, χ_{13} in Eq. (3) may be regarded as χ .

$$\chi_{13} \doteq \chi \quad (9)$$

In the present study the values of $(\partial P/\partial T)_V$ and B were calculated by use of the equation of state, Eq. (10), proposed by Sugie *et al.*¹⁴⁾, which reproduced the experimental values of z for nitrogen¹⁰⁾ within the error of 0.5% under the conditions of 25, 50, and 75°C and up to 500 atm.

$$P = RT/(V + b + c) + aT^{-0.5}/\{(V + c)(V + b + c)\} + dT^2/V + \sum_{j=1}^8 (e_j + f_j T + g_j T^{-2})/V^{j+1} \quad (10)$$

Equation (12) is obtained from Eq. (10) by use of Eq. (11).

$$B = (1/RT) \lim_{\rho \rightarrow 0} (z - 1)/\rho \quad (11)$$

$$B_{SL} = (b - c) - (a/R)T^{-1.5} + (d/R)T + (e_1/R)T^{-1} + (f_1/R) + (g_1/R)T^{-3} \quad (12)$$

The second virial coefficients of nitrogen obtained from Eq. (12), B_{SL} , are shown in **Table 3**. For comparison the values obtained by Michels *et al.*⁴⁾, B_{exp} , are also shown in the table. The results obtained from the Eqs. (7)–(12) are shown in Fig. 1 with the dashed lines. They show better agreement than those obtained from Eq. (4), but the deviation is still large.

Iwasaki⁸⁾ performed with success the theoretical calculation of the viscosity of argon at high pressure, assuming that b_0 might be dependent on temperature. He obtained the following relations by combining Eq. (5) with the virial equation of state:

$$z = PV/RT = 1 + (b_0 - a_0/RT) + b_0\rho(\chi - 1) \quad (13)$$

$$B(T) = b_0(T) - a_0/RT \quad (14)$$

$$C(T_1)/C(T_2) = \{b_0(T_1)/b_0(T_2)\}^2 \quad (15)$$

where $B(T)$, $b_0(T)$, and $C(T)$ imply that B , b_0 , and C

are dependent on temperature T . Then, χ_{13} is obtained from Eqs. (13)–(15) and Eq. (9) by use of the experimental values of z , B , and C .

Since the third virial coefficient of nitrogen presented by Michels *et al.*⁴⁾ showed an irregular temperature dependence, they could not be used in this study. Therefore, the third virial coefficients of nitrogen were determined by use of Eq. (17) derived from Eqs. (10) and (16).

$$C = (1/2RT) \lim_{\rho \rightarrow 0} \partial^2(PV)/\partial \rho^2 \quad (16)$$

$$C_{SL} = (b-c)^2 + \{a(b+2c)/R\}T^{-1.5} + (e_2/R)T^{-1} + (f_2/R) + (g_2/R)T^{-3} \quad (17)$$

The third virial coefficients obtained from Eq. (17), C_{SL} , are shown in Table 3, along with those presented by Michels *et al.*⁴⁾, C_{exp} . The values of b_0 in the temperature range from 0 to 150°C were determined from Eqs. (14) and (15) by using seven sets of $B_{SL}(T)$ and $C_{SL}(T)$ given in Table 3 by means of the least squares method. The theoretical values obtained by this method agree fairly well with those observed as shown in Fig. 1.

Conclusion

The diffusion coefficients of $^{14}\text{CO}_2$ in the CO_2 – N_2 system at high pressure were presented at 25, 50, and 75°C. These data were reproduced by the generalized chart presented by the author. A modified Enskog-Thorne's theory could predict fairly well the diffusion coefficients of a trace of $^{14}\text{CO}_2$ in nitrogen.

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Nomenclature

a	= constant in Eq. (10)	
a_0	= constant in Eq. (5)	
B	= second virial coefficient	[cm ³ /mol]
b	= constant in Eq. (10)	
b_0	= constant in Eq. (5)	
C	= third virial coefficient	[cm ⁶ /mol ²]
c	= constant in Eq. (10)	
D	= diffusion coefficient	[cm ² /sec]
d, e_j, f_j, g_j	= constants in Eq. (10)	
k	= Boltzmann's constant	
M	= molecular weight	[—]
N	= Avogadro's number	
n	= number of molecules per unit volume	[1/cm ³]
P	= pressure	[atm]
R	= gas constant	
T	= temperature	[°K]

t	= temperature	[°C]
V	= molecular volume	[cm ³ /mol]
x	= mole fraction	[—]
z	= compressibility factor	[—]

ϵ	= force constant	
ρ	= density	[mol/cm ³]
σ	= collision diameter	[Å or cm]
χ	= correction factor	[—]
$Q^{(1,1)*}$	= reduced collision integral	[—]

<Subscripts>

1	= radioactive carbon dioxide
2	= normal carbon dioxide
3	= nitrogen
m	= mixture

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