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STUDIES ON THE TRANSPORT PROPERTIES OF FLUIDS AT HIGH PRESSURE

II The Diffusion of $^{14}\text{CO}_2$ in the Carbon Dioxide-Argon and Carbon Dioxide-Methane Systems at High Pressures^{*1)}

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The diffusion coefficients of $^{14}\text{CO}_2$ in the $^{12}\text{CO}_2$ -Ar and $^{12}\text{CO}_2$ - CH_4 system were measured over the pressure range from 15 to 250 atm at 25, 50 and 75°C. The measurements were made through a plug of porous bronze in the diffusion cell using the radioactive tracer technique. In most cases the products of the diffusion coefficient and the density increase slightly with an increase in density in the region of lower density and decrease in the region of higher density. In some systems the products increase consistently with an increase in density under the present experimental conditions. The increase of the products with an increase in density in the binary diffusion is not predicted by Enskog-Thorne's theory, which requires that the products decrease with an increase in density. The values of the products extrapolated to 1 atm agree with the published experimental values and those predicted by Wilke's equation.

Introduction

The diffusion coefficient of gases at high pressures is not only an interesting physical property from the standpoint of the kinetic theory of gases, but also it is an important property for the analysis of the operations and the design of the apparatus in the chemical industry. Enskog^{1,2)} made some theoretical studies of the diffusion process in developing his kinetic theory on non-uniform gases, based on the assumption of a rigid spherical molecule. Slattery *et al.*³⁾ prepared a generalized chart for the self-diffusion coefficient of gases at high densities using Enskog's theoretical relations on the transport properties and the experimental data on the viscosity.

There have been some recent reports⁴⁾ on the gaseous diffusion coefficient at high densities meas-

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- *1) The self-diffusion coefficient of carbon dioxide was published in *Bull. Chem. Soc. Japan*, **39**, 2105 (1966) and the diffusion of $^{14}\text{CO}_2$ in the $^{12}\text{CO}_2$ -Ar system is in print in *Bull. Chem. Soc. Japan*, **41**, 1573 (1968).
- 1) S. Chapman and T. G. Cowling, "The Mathematical Theory of Non-Uniform Gases," Cambridge University Press, London (1939)
 - 2) J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley & Sons, Inc., New York (1954)
 - 3) J. Slattery and R. B. Bird, *A. I. Ch. E. Journal*, **4**, 137 (1948)
 - 4) K. D. Timmerhaus and H. G. Drickamer, *J. Chem. Phys.*, **19**, 1242 (1941); W. L. Robb and H. G. Drickamer, *ibid.*, **19**, 1504 (1951); K. D. Timmerhaus and H. G. Drickamer, *ibid.*, **20**, 981 (1952); Q. R. Jeffries and H. G. Drickamer, *ibid.*, **21**, 1358 (1953), *ibid.*, **22**, 436 (1954); H. A. O'Hern and J. J. Martin, *Ind. Eng. Chem.*, **47**, 2081 (1955); C. Chou and J. J. Martin, *ibid.*, **49**, 758 (1957); E. W. Becker, W. Vogell and F. Zigan, *Z. Naturforsch.*, **8a**, 686 (1953); T. R. Mifflin and C. O. Bennet, *J.*

ured by the use of either the radioactive or the stable isotope-tracer technique. However, the results have not indicated a definite relation between $D\rho$ and ρ (D : diffusion coefficient, ρ : density). For example, in the case of the self-diffusion coefficient of carbon dioxide, Drickamer *et al.* concluded that $D\rho$ decreases in accordance with Enskog's theory until $\rho=0.067$ g/cc, whereas O'Hern *et al.* stated that $D\rho$ is constant and independent of the density, and Becker *et al.* showed that $D\rho$ increases with an increase in density.

The measurements of the diffusion coefficient of $^{14}\text{CO}_2$ in the $^{12}\text{CO}_2$ —Ar and $^{12}\text{CO}_2$ — CH_4 systems, by a method similar to that of O'Hern *et al.*, will be reported here. These measurements were made at the temperatures of 25, 50 and 75°C in the pressure range from 15 to 250 atm. The results will be compared with the values calculated from Enskog's equation, the generalized chart and Wilke's equation⁵⁾.

Experimentals

Apparatus

The diffusion cell, the major part of the apparatus, was nearly identical with that used by O'Hern *et al.*, Mifflin *et al.* and Durbin *et al.* as is shown in Fig. 1. The principle of the method was as follows: a diffusion path, B, composed of porous metal was placed between the two chambers, C and D, equal in volume. The concentration gradient of $^{14}\text{CO}_2$ was created between these two chambers through the porous plug, and the diffusion coefficient of $^{14}\text{CO}_2$, D_{12} , was calculated from the measurement of the change in the concentration of $^{14}\text{CO}_2$ with time.

Each chamber had a volume of 35 cc and was connected with the diffusion path, B, which had a

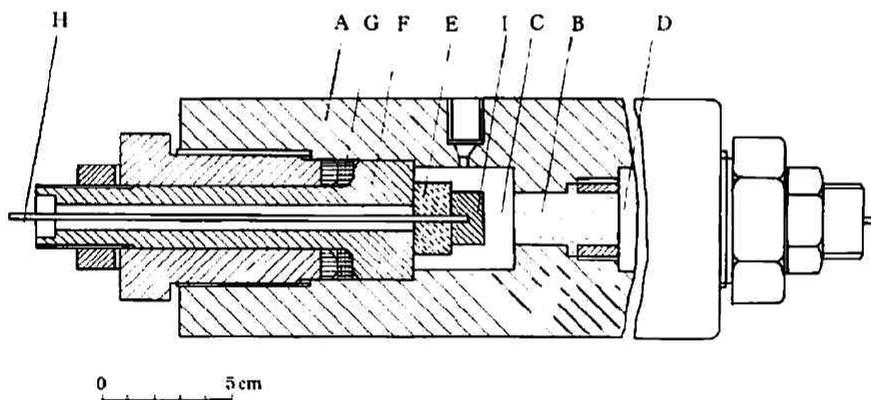


Fig. 1 Diffusion cell

A: body, B: diffusion path, C and D: ionization chamber, E: quartz disk, F: stainless steel plug, G: teflon packing, H: lead-in wire, I: collecting electrode

Chem. Phys., 24, 975 (1958); 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); H. H. Reamer and B. H. Sage, *J. Chem. Eng. Data*, 8, 34 (1963); I. F. Golubev and A. G. Bondarenko, *Gas. Prom.*, 8, 46 (1963)

5) C. R. Wilke, *Chem. Eng. Progr.*, 46, 95 (1950)

length of 40 mm and a diameter of 18 mm. The diffusion path was a plug of sintered bronze powder; two types of plugs were used, one with a grain size of ϕ 160~250 μ (I) and the other, with a grain size of ϕ 60~70 μ (II). The concentration of $^{14}\text{CO}_2$ was measured by means of the ionization current in the chamber. The collecting electrode, I (20 ϕ \times 15 mm), was made of invar steel and was insulated from the stainless steel plug, F, by a surface-polished quartz disk, E (30 ϕ \times 15 mm). The collecting electrode, the quartz disk, and the plug were cemented together with epoxy resin. The quartz disk had a hole of 3 mm in diameter in its center through which the lead-in wire, H, used for measuring the ionization current, projected. The lead-in wire was insulated from the steel pipe, not shown in Fig. 1, with methacrylate resin insulators and was connected with a dynamic condenser electrometer manufactured by the Okura Electric Co. Ltd. The applied voltage was maintained at about 540 V, using 12 layer-built dry cells of 45 V each. The quantity of $^{14}\text{CO}_2$ used for each measurement was in the range from 0.01 to 1 μ Ci, and the ionization current was in the range from 10^{-13} to 10^{-11} A.

The diffusion cell was mounted in an air thermostat, the temperature of which was kept constant within $\pm 0.1^\circ\text{C}$. The temperature of the cell was measured by means of copper-constantan thermocouples inserted in the holes (2.2 ϕ \times 20 mm deep) drilled at six points round the chambers. The pressure was measured by a Bourdon gauge calibrated against a pressure balance of a free-piston type. The errors in pressure measurements were within ± 0.02 atm up to 20 atm, ± 0.1 atm in the range from 20 to 50 atm, and ± 0.5 atm in the range from 50 to 250 atm.

Materials

The radioactive $^{14}\text{CO}_2$ was generated by adding 60 per cent HClO_4 to $\text{Ba}^{14}\text{CO}_3$; its specific radioactivity was approximately 1 μ Ci/cc at N.T.P. The non-radioactive carbon dioxide, with a purity of over 99.9 per cent and with a water content of less than 0.04 per cent, was used after it had been dried over silica gel. Argon and methane, with a purity of 99.99 and 99.9 per cent, respectively, were used without further purification. Bulk mixtures of normal carbon dioxide—argon and normal carbon dioxide—methane were prepared in storage cylinders. Their exact compositions were determined by bubbling samples through a potassium hydroxide solution. For the present investigation the mixtures are not in the liquid state⁶⁾.

Procedure

The arrangement of the experimental apparatus is shown in Fig. 2. The temperature of the diffusion cell, A, was kept constant throughout the experiment within $\pm 0.02^\circ\text{C}$. The difference among the temperatures given by the six thermocouples described above never exceeded 0.02°C . After bringing the cell to the desired temperature, the cell was evacuated to approximately 10^{-2} mmHg by means of a vacuum pump, F. A suitable quantity of $^{14}\text{CO}_2$ was introduced through the gas burette, E, from the $^{14}\text{CO}_2$ container, D, into the left chamber in the cell. The non-radioactive pure gases or mixtures were introduced into the right chamber from the cylinder, G, through the drying tube, H, and compressed to the desired pressure by the oil pump, J. In this way a major portion of the $^{14}\text{CO}_2$ was collected in the left chamber and a large concentration gradient of $^{14}\text{CO}_2$ was established between the two chambers through the porous plug. Then, the cell was disconnected from the pressure system between the valves,

6) G. Kaminishi, *Private communication*

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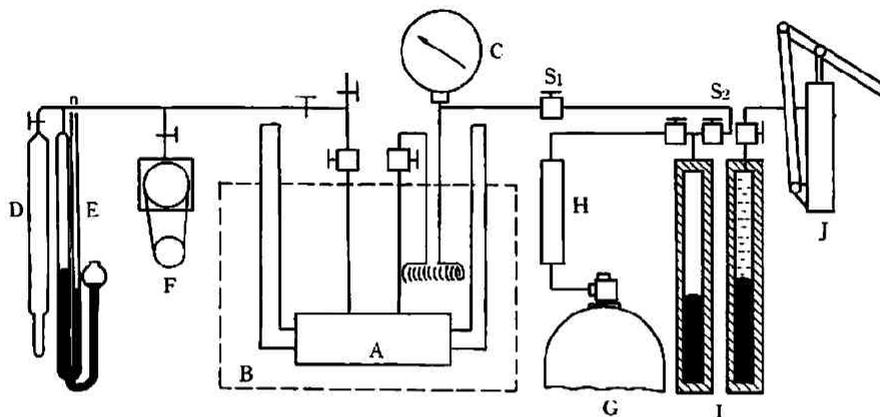


Fig. 2 Schematic diagram of apparatus

A: diffusion cell, B: air thermostat, C: pressure gauge, D: $^{14}\text{CO}_2$ container, E: gas burette, F: vacuum pump, G: $^{12}\text{CO}_2$ cylinder, H: drying tube, I: intensifier, J: oil pump, S_1 and S_2 : valves

S_1 and S_3 , and the voltage was applied to the cell; the resulting ionization currents were measured and recorded. An example is shown in Fig. 3.

The proportionality between the ionization current and the concentration of $^{14}\text{CO}_2$, essential for the quantitative treatment of the diffusion data, was confirmed experimentally in pure carbon dioxide, argon, methane, and each mixture at several constant temperatures and pressures. The experimental procedure

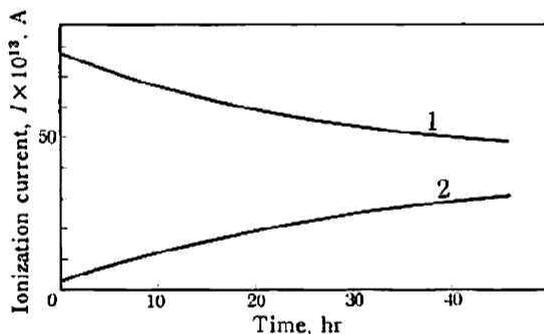


Fig. 3 The variation of the ionization current with time at 50°C , 84.2 atm for the diffusion of $^{14}\text{CO}_2$ in normal carbon dioxide
1: I_1 , 2: I_2

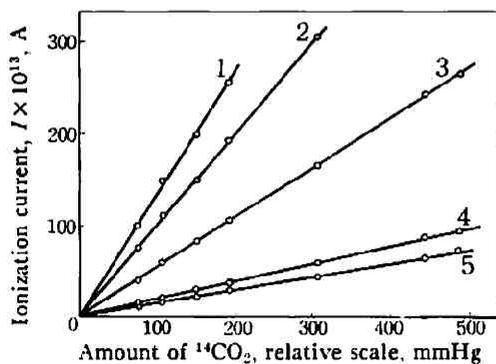


Fig. 4 Relations between the amount of $^{14}\text{CO}_2$ and the ionization current at 50°C in normal carbon dioxide
1: 10 atm, 2: 20 atm, 3: 50 atm, 4: 100 atm, 5: 200 atm

was as follows: after the ionization chamber had been evacuated, a mixture of $^{14}\text{CO}_2$ and $^{12}\text{CO}_2$ was introduced into the chamber up to 7~500 mmHg. These pressures are shown as abscissa in Fig. 4. The amounts of $^{14}\text{CO}_2$ are proportional to these pressures. Then, the pressure of the chamber was raised to 10~250 atm by introducing normal carbon dioxide, argon, methane and mixtures, and the ionization current was measured. For example, the results for carbon dioxide at 50°C are shown in Fig. 4.

Calculation

Assuming that the concentration gradient of $^{14}\text{CO}_2$ in the diffusion path is linear and that the concentration in each chamber is uniform, the following equations are obtained:

$$\ln(C_1 - C_2) = -KD_{12}t + \text{constant} \quad (1)$$

$$K = \frac{A}{L} \left(\frac{1}{V_1} + \frac{1}{V_2} \right) \quad (2)$$

where C_1 and C_2 are the concentrations of $^{14}\text{CO}_2$ in the chambers 1 and 2, shown as C and D, respectively, in Fig. 1. D_{12} is the mutual diffusion coefficient of $^{14}\text{CO}_2$, and t is the time. K is an apparatus constant: it is given by equation (2), where A and L are the effective cross section and the effective length of the diffusion path, and V_1 and V_2 are the volumes of the chambers 1 and 2, respectively. Since a proportionality holds between the concentration of $^{14}\text{CO}_2$ and the ionization current, equation (1) may be written as follows:

$$\ln \Delta I = -KD_{12}t + \text{constant}, \quad (3)$$

$$\Delta I = I_1 - \gamma I_2,$$

$$\gamma = \frac{I'_1}{I'_2}$$

where I_1 and I_2 are the ionization currents in the chambers 1 and 2, respectively. I'_1 and I'_2 are the ionization currents in the chambers 1 and 2, respectively, when $^{14}\text{CO}_2$ is introduced into the chambers at the same concentration. According to equation (3) $\ln \Delta I$ should be linear with t : this was experimentally proved, as is shown in Fig. 5, where the common logarithms are used. It should be noted that the plot of $\log \Delta I$ against t presented a concave curve when the type-I porous plug was used at higher pressures than 100 atm and the assumption made for the derivation of equation (1) became

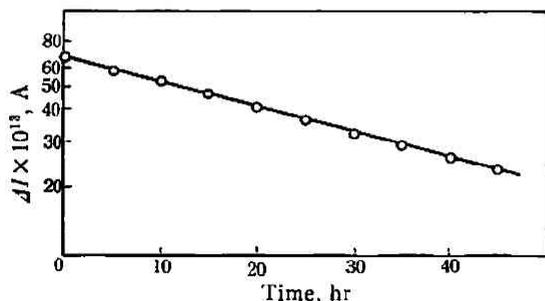


Fig. 5 Semi log plot of the current difference ΔI vs. time at 50°C, 84.2 atm for the diffusion of $^{14}\text{CO}_2$ in normal carbon dioxide

invalid. However, a type-II porous plug gave no such trouble during the experiments at higher pressures.

If ΔI at time t_i and t_f are designated as $(\Delta I)_i$ and $(\Delta I)_f$, respectively, KD_{12} can be calculated by the following equation:

$$KD_{12} = \frac{6.3961 \times 10^{-4}}{\Delta t} \log \frac{(\Delta I)_i}{(\Delta I)_f} \quad (4)$$

where the terms are expressed as follows: K ; $1/\text{cm}^2$, D ; cm^2/sec , Δt ; hr, and ΔI ; A.

Hutchinson⁷ verified the following relationship between the self-diffusion coefficient, D_{11} , and the mutual diffusion coefficient, D_{12} , at the normal pressure:

$$\frac{D_{11}}{D_{12}} = \left[\left(\frac{m_1 m_2}{m_1 + m_2} \right) \left(\frac{m_1 + m_2}{m_1 m_2} \right) \right]^{\frac{1}{2}} = \left(\frac{2m_2}{m_1 + m_2} \right)^{\frac{1}{2}} \quad (5)$$

where m_1 and m_2 are masses of the gaseous molecular species containing isotopes. Assuming that the above relationship holds in the high pressure region, the self-diffusion coefficient of normal carbon dioxide, D_{11} , was obtained by multiplying the D_{12} measured in the present work by 1.011.

Determination of Apparatus Constant

The apparatus constant, K , is given by equation (2). However, the effective cross section and length, A and L , of a porous diffusion path are not known and the volumes of the two chambers, V_1 and V_2 , are not precisely known. Therefore, the apparatus constant was experimentally determined at each temperature as follows.

The apparatus constant, K_1 , when a type-I porous plug was used

The diffusion coefficient of $^{14}\text{CO}_2$ in normal carbon dioxide, D_{12} , was measured in the pressure range from 2 to 50 atm by using a type-I porous plug as a diffusion path. The values of $K_1 D_{11} P$ ob-

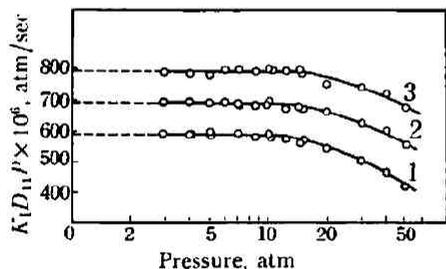


Fig. 6 Relations between $K_1 D_{11} P$ and pressure
1: 25°C, 2: 50°C, 3: 75°C

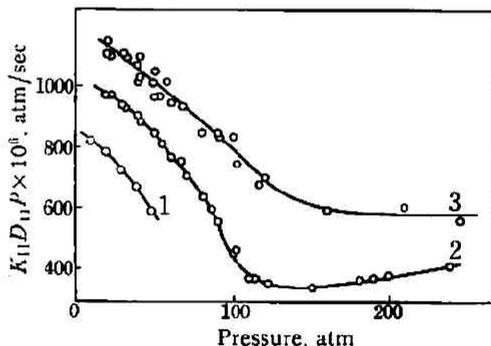


Fig. 7 Relations between $K_{11} D_{11} P$ and pressure
1: 25°C, 2: 50°C, 3: 75°C

7) F. Hutchinson, *J. Chem. Phys.*, 17, 1081 (1949)

tained by applying a mass correction to D_{12} are shown in Fig. 6. The values of $K_I D_{11} P$ at 1 atm were obtained by extrapolation using the observed values of $K_I D_{11} P$. K_I was determined by the use of the values of D_{11} reported by Amdur *et al.*⁸⁾ at 1 atm. These are shown in Table 1. The smoothed values of D_{11} obtained by using the values of K_I are shown in Table 2. The deviation of the experimental values from the smoothed one reaches a maximum of 3.6 per cent.

Table 1 Determination of apparatus constant, K_I

Temp. °C	P atm	$K_I D_{11} P \times 10^6$ atm/sec	$D_{11} \times 10^3$ [*] cm ² /sec	$K_I \times 10^3$ l/cm ²
25	1.0	591	114.0	5.19
50	1.0	689	132.7	5.20
75	1.0	795	152.3	5.22

* Measured by Amdur *et al.*⁸⁾

Table 2 Smoothed values of $D_{11} \times 10^3$, cm²/sec for the self-diffusion of normal carbon dioxide

P , atm	25°C	50°C	75°C
10.0	11.2	13.2	15.2
20.0	5.30	6.35	7.48
30.0	3.26	4.06	4.81
40.0	2.25	2.90	3.51
50.0	1.62	2.18	2.71

The apparatus constant, K_{II} , when a type-II porous plug was used

The values of $K_{II} D_{11} P$ obtained experimentally for the self-diffusion of normal carbon dioxide at 25°C in the pressure range from 20 to 50 atm and at 50 and 75°C in the range from 20 to 250 atm are shown in Fig. 7. The smoothed values are shown in Table 3. The values of K_{II} calculated by using the D_{11} values in Table 2 are shown in the last column of Table 3. The type-II porous plug was used through the measurements in the pressure range from 15 to 250 atm for the diffusion of ¹⁴CO₂ in argon, methane and mixtures.

Results and Discussion

According to Enskog-Thorne's theory assuming a rigid sphere as a molecular model, the mutual diffusion coefficient of gases, D_{12} , at high pressures is given by equation (6).

$$D_{12} = \frac{(D_{12})^\circ}{\lambda_{12}} \quad (6)$$

$$(D_{12})^\circ = \frac{3}{16} \sqrt{\frac{2kT}{\pi\mu}} \cdot \frac{1}{n\sigma^2 D^{(1,1)^\circ}} \quad (7)$$

$$\lambda_{12} = 1 + \frac{\pi}{12} n_1 \sigma_1^3 \left(8 - \frac{3\sigma_1}{\sigma_{12}} \right) + \frac{\pi}{12} n_2 \sigma_2^3 \left(8 - \frac{3\sigma_2}{\sigma_{12}} \right) \quad (8)$$

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

For the self-diffusion coefficient these equations are reduced to the following equations.

$$D_{11} = \frac{(D_{11})^\circ}{\chi} \quad (6')$$

$$(D_{11})^\circ = \frac{3}{8} \sqrt{\frac{kT}{\pi m}} \cdot \frac{1}{n\sigma^2 \Omega^{(1,1)*}} \quad (7')$$

$$\chi = 1 + 0.625 \left(\frac{2}{3} \pi n \sigma^3 \right) + 0.2569 \left(\frac{2}{3} \pi n \sigma^3 \right)^2 + 0.115 \left(\frac{2}{3} \pi n \sigma^3 \right)^3 + \dots \quad (8')$$

where $(D_{12})^\circ$ is the value which can be calculated from the relationship applicable to the diffusion at the normal pressure and approximately given by equation (7), χ is the correction factor due to the pressure rise, k is Boltzmann's constant, μ is the reduced mass, m is the mass of the molecule, n is the number density of the molecules, $\Omega^{(1,1)*}$ is the reduced collision integral, and σ is a constant related to the intermolecular potential. The subscripts 1 and 2 denote the molecules 1 and 2, respectively. It can be seen from equation (7) that $(D_{12})^\circ n$ or $(D_{12})^\circ \rho$ (ρ : mole/l) is a function of temperature alone in the vicinity of the normal pressure. However, according to equation (6), $D_{12} \rho = (D_{12})^\circ \rho / \chi_{12}$ and $D_{12} \rho$ is dependent not only on the temperature, but also on χ_{12} , that is, on ρ . Therefore, it is convenient to study the relationship between $D_{12} \rho$ and ρ .

The self-diffusion coefficient of carbon dioxide

In Fig. 8, $D_{11} \rho$ is plotted against ρ . The values of ρ were calculated by using the compressibility

Table 3 Determination of apparatus constant, K_{11}

P atm	$K_{11} D_{11} P \times 10^6$ atm/sec	$K_{11} \times 10^3$ 1/cm ²
25°C		
10	826	7.38
20	783	7.39
30	732	7.48
40	669	7.43
50	587	7.25
average		7.39
50°C		
20	970	7.64
30	930	7.65
40	880	7.59
50	830	7.61
average		7.62
75°C		
20	1130	7.55
30	1090	7.57
40	1050	7.49
50	1005	7.42
average		7.51

data of Michels *et al.*⁹⁾ The plot shows a close similarity to that of the results obtained by O'Hern *et al.* The values at 35°C. which were interpolated from our experimental values, were always higher than their experimental values, but the differences were never more than 5 per cent. On the other hand, there were large deviations in the experimental values of Drickamer *et al.*, and so their values could not be used for an accurate comparison. The relative values of $D_{11}\rho$, obtained by Becker *et al.*, were expressed as 1.00 at 20°C and 15 atm, 1.08 at 40 atm, and 1.26 at 50 atm, and they showed a rapid increase with an increase in pressure, thus indicating an entirely different tendency from the results obtained by the present investigation.

The values calculated by substituting $\sigma = 3.996 \text{ \AA}$ in equation (8') are shown as dashed lines in Fig. 8. The deviations increase with an increase in pressure, amounting approximately to 50 per cent when $\rho = 10 \text{ mole/l}$. Even if the decrease in σ with an increase in pressure was taken into account in equation (8'), in accordance with the consideration of O'Hern *et al.*, a theoretical relation which fits the experimental values could not be obtained.

The values of $D_{11}P$ calculated from the generalized chart are shown as solid lines in Fig. 9. The deviation from present experimental values is approximately 20 per cent in the vicinity of 50 atm, but decreases in the high pressure region.

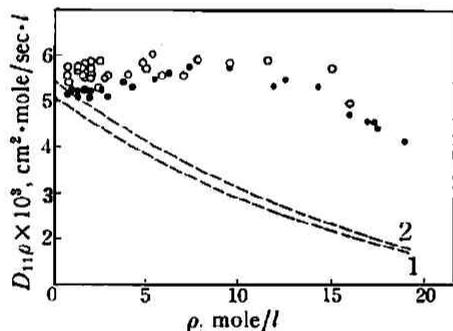


Fig. 8 Comparison of the measured values with the values calculated by Enskog's theory for the self-diffusion of carbon dioxide
Experimental: ●—50°C, ○—75°C.
Theoretical: 1—50°C, 2—75°C.

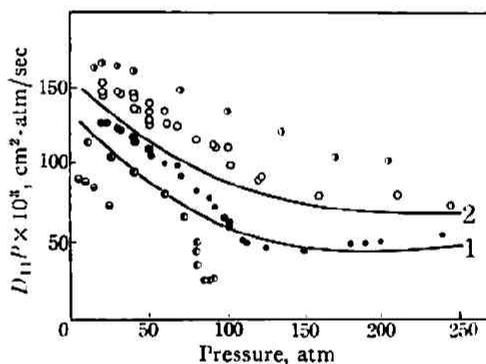


Fig. 9 Comparison of the measured values with the values calculated by the generalized chart for the self-diffusion of carbon dioxide
Present work: ●—50°C, ○—75°C,
O'Hern *et al.*: ●—100°C, ○—35°C,
●—0°C.
Calculated: 1—50°C, 2—75°C.

The diffusion coefficient of $^{14}\text{CO}_2$ in argon, methane and the binary mixtures with carbon dioxide

In Figs. 10 and 11, $D_{12}\rho$ are plotted against ρ . The density, ρ , for argon was calculated from the compressibility factors obtained by Michels *et al.*¹⁰⁾ The densities for carbon dioxide—argon mixtures

9) A. Michels and C. Michels, *Proc. Roy. Soc.*, A153, 201 (1936); A160, 348 (1937)

10) A. Michels, Hub. Wijker and HK Wijker, *Physica*, 15, 627 (1949)

were calculated by using the compressibility chart*2) with pseudo-critical temperature T_c and pressure P_c obtained by the following relations:

$$T_c = x_2(T_c)_2 + x_3(T_c)_3 \quad (9)$$

$$P_c = x_2(P_c)_2 + x_3(P_c)_3 \quad (10)$$

where the subscripts 2 and 3 denote normal carbon dioxide and argon. The density calculated above agrees within 2.1 per cent with that calculated from Abraham's data¹²⁾, which range from 50 to 1,000 atm at 50°C. It may be noted that the maximum deviation of the values calculated by using Weber's chart from that calculated by using Abraham's data is 4.6 per cent. The densities for methane were calculated from the compressibility factors obtained by Kvalnes *et al.*¹³⁾ The densities for carbon dioxide—methane mixtures were calculated from the compressibility factors obtained by Reamer *et al.*¹⁴⁾

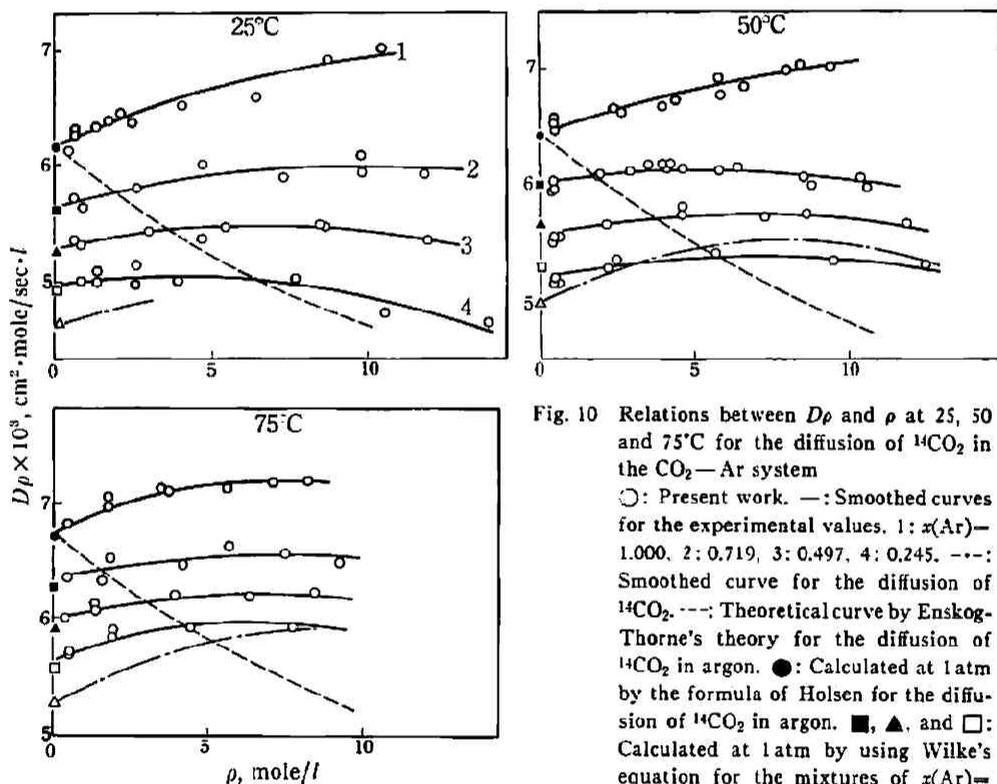


Fig. 10 Relations between $D\rho$ and ρ at 25, 50 and 75°C for the diffusion of $^{14}\text{CO}_2$ in the CO_2 —Ar system

○: Present work. —: Smoothed curves for the experimental values. 1: $x(\text{Ar})=1.000$, 2: 0.719, 3: 0.497, 4: 0.245. ---: Smoothed curve for the diffusion of $^{14}\text{CO}_2$. ---: Theoretical curve by Enskog-Thorne's theory for the diffusion of $^{14}\text{CO}_2$ in argon. ●: Calculated at 1 atm by the formula of Holsen for the diffusion of $^{14}\text{CO}_2$ in argon. ■, ▲, and □: Calculated at 1 atm by using Wilke's equation for the mixtures of $x(\text{Ar})=$

0.719, 0.497, and 0.245, respectively. △: Calculated at 1 atm from the experimental values of Arndur for the diffusion of $^{14}\text{CO}_2$ in normal carbon dioxide.

*2) This chart was prepared from the compressibility data for carbon dioxide and argon using the same method as Weber's generalized compressibility chart¹¹⁾.

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

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

13) H. M. Kvalnes and V. L. Gaddy, *J. Am. Chem. Soc.*, 53, 394 (1931)

14) H. H. Reamer, R. H. Olds, R. H. Sage and W. N. Lacey, *Ind. Eng. Chem.*, 36, 88 (1944)

The values of $D_{12}\rho$ at unit mole fraction of argon and methane are equivalent to the binary diffusion coefficients of the $^{14}\text{CO}_2\text{—Ar}$ and $^{14}\text{CO}_2\text{—CH}_4$ systems. The extrapolation of these products to 1 atm provides a basis for comparison with the low-pressure experimental results by other investigators. The formulae of the experimental binary diffusion coefficient at 1 atm were presented for $^{12}\text{CO}_2\text{—Ar}$ system by Holsen *et al.*¹⁵⁾ and for the $^{12}\text{CO}_2\text{—CH}_4$ system in International Critical Tables¹⁶⁾. These formulae yielded the values which were in agreement with the extrapolated values of the present investigation.

The effect of density (or pressure) on the binary diffusion coefficient may be predicted by equation (6), which is the only theoretical equation offering any practical application. It is convenient to express as follows:

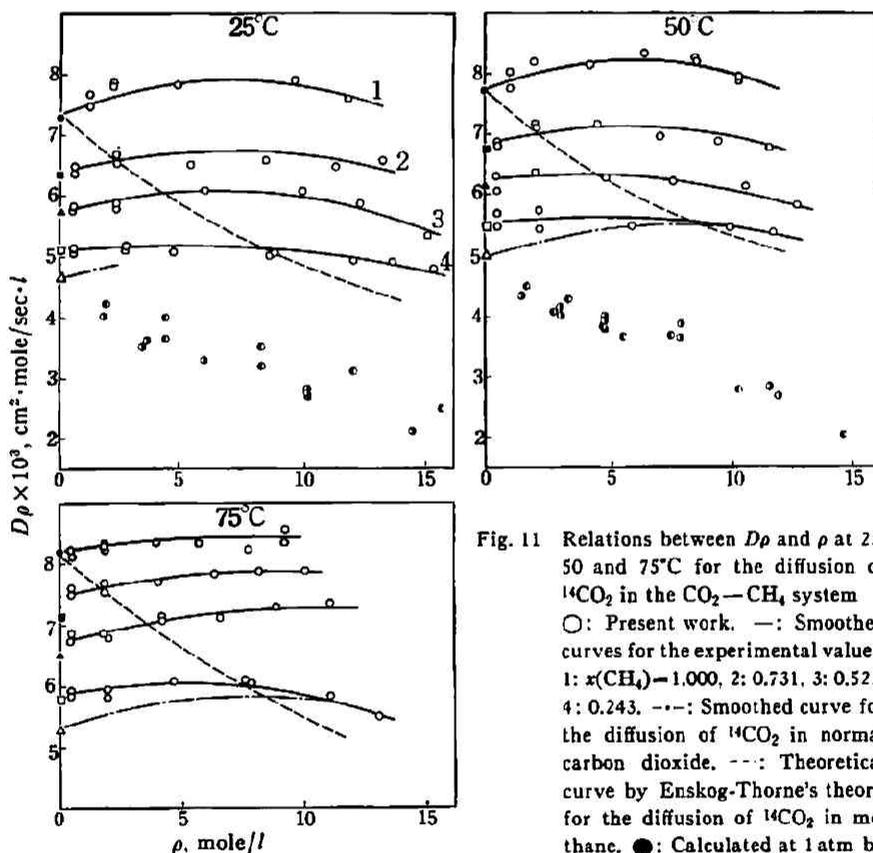


Fig. 11 Relations between $D\rho$ and ρ at 25, 50 and 75°C for the diffusion of $^{14}\text{CO}_2$ in the $\text{CO}_2\text{—CH}_4$ system

○: Present work. —: Smoothed curves for the experimental values, 1: $x(\text{CH}_4)=1.000$, 2: 0.731, 3: 0.522, 4: 0.243. ---: Smoothed curve for the diffusion of $^{14}\text{CO}_2$ in normal carbon dioxide. - - -: Theoretical curve by Enskog-Thorne's theory for the diffusion of $^{14}\text{CO}_2$ in methane. ●: Calculated at 1 atm by

the equation given in the International Critical Tables for the diffusion of $^{14}\text{CO}_2$ in methane. ■, ▲, and □: Calculated at 1 atm by using Wilke's equation for the mixtures of $x(\text{CH}_4)=0.731$, 0.522, and 0.243, respectively. △: Calculated at 1 atm from the experimental values of Armdur for the diffusion of $^{14}\text{CO}_2$ in normal carbon dioxide. ◐ and ◑: The experimental values reported by Jeffries and Drickamer (1954) for $x(\text{CH}_4)=0.25$ and 0.50.

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

16) "International Critical Tables," Vol. V, p. 62 (1929)

$$D_{13}\rho = \frac{(D_{13})^{\circ}\rho}{z_{13}} \quad (11)$$

$$z_{13} = 1 + 0.2618n_3\sigma_3^3 \left(8 - \frac{3\sigma_3}{\sigma_{13}} \right) \quad (12)$$

where the subscript 1 denotes radioactive carbon dioxide and subscript 3 denotes argon or methane. The empirical combining law $\sigma_{13} = (\sigma_1 + \sigma_3)/2 \approx (\sigma_2 + \sigma_3)/2$ was employed in the calculation where the subscript 2 denotes normal carbon dioxide. The collision diameters $\sigma_2 = 3.996\text{\AA}$ and $\sigma_3 = 3.418\text{\AA}$ for argon and $\sigma_3 = 3.882\text{\AA}$ for methane, being taken from Ref. 2) are those determined from the viscosity measurement for Lennard-Jones model. $(D_{13})^{\circ}$ was calculated by using the formulae published in Refs. 15) and 16) with mass correction. As shown in Figs. 10 and 11 by dashed lines, the theory requires the products $D_{13}\rho$ to decrease with an increase in density. The calculated products are low by about 30 per cent at a density of 8 mole/l at each temperature. Their poor agreement is in accordance with most of the other high pressure diffusion results.

It has been shown by Wilke *et al.*²⁵⁾ that at low pressures the effective diffusion coefficient D of a trace component "i" in a gas mixture is given by the equation:

$$\frac{1}{D} = \sum_{j \neq i} \frac{x_j}{D_{ij}} \quad (13)$$

where x_j is the mole fraction and D_{ij} is the binary diffusion coefficient. This equation was confirmed by several recent experimental investigations¹⁷⁾.

According to equation (13), the effective diffusion coefficient D of a trace component ($^{14}\text{CO}_2$) in the gas mixture is given by the equation:

$$\frac{1}{D} = \frac{x_2}{D_{12}} + \frac{x_3}{D_{13}} \quad (14)$$

where D_{12} is the binary diffusion coefficient of $^{14}\text{CO}_2$ in normal carbon dioxide and D_{13} is the diffusion coefficient of $^{14}\text{CO}_2$ in argon or methane. 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} ⁸⁾, and the binary diffusion coefficients in the $^{12}\text{CO}_2$ —Ar¹⁵⁾ or $^{12}\text{CO}_2$ —CH₄¹⁶⁾ systems, D_{23} . The calculated values of $D\rho$ at 1 atm thus obtained for intermediate concentrations are shown in Figs. 10 and 11. These calculated values are in agreement with the extrapolated values.

At high pressures much less is known about diffusion in the multicomponent system either theoretically or experimentally. Recently, a few studies of high pressure diffusion with the ternary systems, $^{14}\text{CO}_2$ — $^{12}\text{CO}_2$ —CH₄, $^{14}\text{CO}_2$ — $^{12}\text{CO}_2$ —H₂, and $^{14}\text{CO}_2$ — $^{12}\text{CO}_2$ —C₃H₈ have been made⁴⁾.

Enskog-Thorne's theory has not been extended to the ternary systems at high pressures. Therefore, the applicability of equation (14) to the high pressure diffusion coefficient was tested in the form

$$\frac{1}{D\rho} = \frac{x_2}{(D_{12}\rho)} + \frac{x_3}{(D_{13}\rho)} \quad (15)$$

$$x_2 + x_3 \approx 1$$

17) 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**, 1325 (1968)

where D , D_{12} and D_{13} are the values at density ρ . Equation (15) indicates that $1/(D\rho)$ may vary linearly with either x_2 or x_3 . $D=D_{12}$ at $x_2=1$, and $D=D_{13}$ at $x_3=1$. The values of $D\rho$ were read from the smoothed curves in Figs. 10 and 11. For example, the values of $1/(D\rho)$ at 50°C have been plotted against the mole fraction of argon or methane, x_3 , at 1 atm and $\rho=2, 6$ and 10 mole/l in Figs. 12 and 13. The plots are straight lines at 1 atm. At higher densities they are convex curves for the CO_2 —Ar system and have a flexion at $x_3 \approx 0.25$ for the CO_2 — CH_4 system.

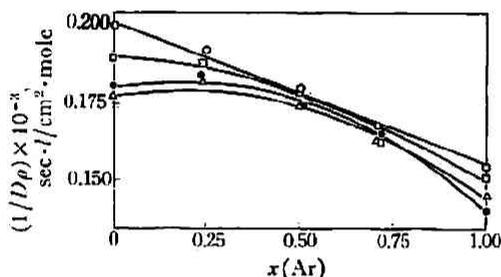


Fig. 12 Relations between $1/(D\rho)$ and $x(\text{Ar})$ at 50°C for the diffusion of $^{14}\text{CO}_2$ in the CO_2 —Ar system
○: 1 atm, □, △, and ●: 2, 6, and 10 mole/l, respectively

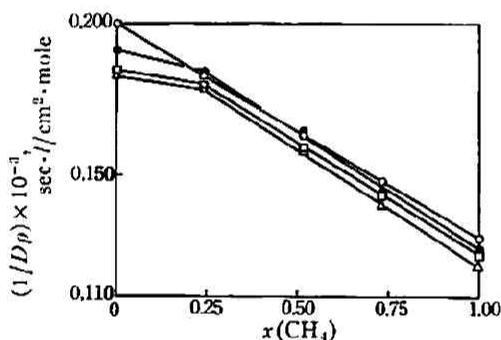


Fig. 13 Relations between $1/(D\rho)$ and $x(\text{CH}_4)$ at 50°C for the diffusion of $^{14}\text{CO}_2$ on the CO_2 — CH_4 system
○: 1 atm, □, △, and ●: 2, 6, and 10 mole/l, respectively

The values of $D\rho$ obtained by Jeffries *et al.* are shown in Fig. 11. They are lower than the values of $D\rho$ obtained by the present investigation and independent of the composition of the mixtures and decrease consistently with an increase in density in accordance with Enskog-Thorne's theory for the self-diffusion coefficient of carbon dioxide. These differences may be due to the difference of the experimental method, but seem to be too large. Thus, further investigation will be necessary in order to clarify the effect of density and composition on the diffusion in the high pressure range.

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