Ternary Diffusion in the ^{20}Ne–^{22}Ne–CO_2 System

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Self-diffusion coefficients of CO_2 of the binary system of Ne and CO_2 were measured for the whole composition range at 25°C under 760 mmHg. The system was also analysed as a ternary system of ^{20}Ne, ^{22}Ne, and CO_2. The isotope separation of ^{20}Ne and ^{22}Ne during the course of diffusion was measured and analyzed by means of the ternary diffusion equations obtained by an extension of Darken's binary diffusion equation. The experimentally observed $^{22}Ne/^{20}Ne$ ratios agreed well with the values calculated by the equations. The results show that the concept of the intrinsic diffusion flux density, introduced by Darken for binary diffusion, is valid and applicable to ternary diffusion in the gaseous system.

Darken derived the following equation for the binary diffusion in a thermodynamically ideal system[1] in order to explain the Kirkendall effect which takes place in interdiffusion of a binary metallic alloy:

$$J_i = -D_i\frac{\partial C_i}{\partial x} + C_i v \tag{1}$$

where J is the diffusion flux density, D the intrinsic diffusion coefficient, C molar concentration, v the velocity of mass flow, and subscript i refers to component i. Eq. (1) is defined with respect to the volume center reference frame. It also holds with respect to the cell-fixed reference frame in the case where partial molar volumes of the respective components remain constant, *viz.*,

$$\sum C_i = C_0 = \text{constant} \tag{2}$$

The first term in Eq. (1) is the diffusion flux density relative to the mass flow velocity and is called intrinsic diffusion flux density. The magnitude of v is equal to the sum of intrinsic diffusion flux densities of both components, *i. e.* the difference of their absolute values, and can be represented by

$$v = \frac{1}{C_0}\left(D_1\frac{\partial C_1}{\partial x} + D_2\frac{\partial C_2}{\partial x}\right) \tag{3}$$

Substituting Eq. (3) in Eq. (1), Darken obtained

$$J_i = -(N_2D_1 + N_1D_2)\frac{\partial C_i}{\partial x} \tag{4}$$

where N_i is the mole fraction of the ith component. He also derived the following binary diffusion equation for a nonideal system:

$$J_i = -(N_2D_1 + N_1D_2)\frac{\partial C_i}{\partial x}\left(1+\frac{\mathrm{d}\ln\gamma_i}{\mathrm{d}\ln N_i}\right) \tag{5}$$

where γ_i is the activity coefficient of the ith component on the mole fraction basis.

Darken's binary diffusion equations have been tested with many metallic alloy systems, but the lack of thermodynamical information on metallic alloys has made quantitative validity of the equations ambiguous. Some binary organic liquid systems showed the validity of Darken's equation quantitatively[2] but not others.[3]

If Darken's analysis is sound for binary diffusion, it could be extended to ternary diffusion and also to general multicomponent diffusion. The purpose of present work is to confirm experimentally the validity of ternary diffusion equation obtained by extending Darken's binary diffusion equation.

In order to avoid a complex effect of thermodynamical nonideality, gaseous systems are utilized. The Kirkendall effect also was experimentally demonstrated for binary diffusion of gaseous system.[4]

We have employed the ^{20}Ne–^{22}Ne–CO_2 system. Validity of the derived ternary diffusion equations was confirmed by comparing the experimental gaseous compositions with the calculated ones for interdiffusion between CO_2 and mixture of ^{20}Ne and ^{22}Ne by a diaphragm-cell method.

Theoretical

A. Ternary Diffusion Equations in Terms of Intrinsic Diffusion Coefficients. If the system is thermodynamically ideal, Eq. (1) can also be applied to ternary diffusion. In this case, Eq. (3) should be replaced by the following equation.

$$v = \frac{1}{C_0}\left(D_1\frac{\partial C_1}{\partial x} + D_2\frac{\partial C_2}{\partial x} + D_3\frac{\partial C_3}{\partial x}\right) \tag{6}$$

If Eq. (2) also holds in a ternary system, we obtain

$$\sum\frac{\partial C_i}{\partial x} = 0 \tag{7}$$

Substitution of Eq. (6) in Eq. (1) with the use of Eq. (7) leads to

$$\left.\begin{aligned} J_1 &= -D_1\frac{\partial C_1}{\partial x} - N_1\left[(D_1-D_2)\frac{\partial C_2}{\partial x} + (D_1-D_3)\frac{\partial C_3}{\partial x}\right] \\ J_2 &= -D_2\frac{\partial C_2}{\partial x} - N_2\left[(D_2-D_3)\frac{\partial C_3}{\partial x} + (D_2-D_1)\frac{\partial C_1}{\partial x}\right] \\ J_3 &= -D_3\frac{\partial C_3}{\partial x} - N_3\left[(D_3-D_1)\frac{\partial C_1}{\partial x} + (D_3-D_2)\frac{\partial C_2}{\partial x}\right] \end{aligned}\right\} \tag{8}$$

A similar derivation is also applicable to the general multicomponent diffusion, giving

$$J_i = -D_i\frac{\partial C_i}{\partial x} - N_i\sum_{j}^{i\neq j}(D_i-D_j)\frac{\partial C_j}{\partial x} \tag{9}$$

1) L. S. Darken, *Trans. Met. Soc., AIME*, **175**, 184 (1948).

2) R. Mills, *J. Phys. Chem.*, **67**, 600 (1963). L. Miller and P. C. Carman, *Trans. Faraday Soc.*, **55**, 1831 (1959). J. E. Reynolds, B. L. Averbach, and M. Cohen, *Acta Metal.*, **5**, 29 (1957).

3) A. P. Hardt, D. K. Anderson, R. Rathbun, B. W. Mar, and A. L. Babb, *J. Phys. Chem.*, **63**, 2059 (1959). R. R. Irani and R. W. Adamson, *ibid.*, **64**, 199 (1960).

4) E. J. Hellund, *Phys. Rev.*, **57**, 737 (1940). L. Miller and P. C. Carman, *Nature*, **186**, 594 (1960). K. P. McCarty and E. A. Mason, *Phys. Fluids*, **3**, 908 (1960).

Ternary diffusion described by Eqs. (8) is characterized by the curved diffusion path on the ternary composition diagram. In special cases the diffusion path becomes linear on the ternary diagram, the following equations being satisfied.

$$J_1 : J_2 : J_3 = \frac{\partial C_1}{\partial x} : \frac{\partial C_2}{\partial x} : \frac{\partial C_3}{\partial x} \tag{10}$$

The conditions which lead Eqs. (8) to Eq. (10) are as follows:

(i) $D_1=D_2=D_3$.
(ii) $D_1=D_2$ for the diffusion with no concentration gradient for component 3.
(iii) $D_1=D_2$ for the diffusion between two compositions with an equal ratio of concentrations 1 and 2.

If D_1 is greater than D_2 in the diffusion between two compositions with an equal ratio of two concentrations, the diffusion path is curved in an S shape on the ternary diagram as shown schematically in Fig. 1. If D_1 is smaller than D_2, the diffusion path should be in a reversed S shape.

The greater the difference between the two diffusion coefficients or the smaller the value of D_3 than of the other two, the more curved the diffusion path on the diagram. Detailed characteristics of ternary diffusion have been discussed elsewhere.[5]

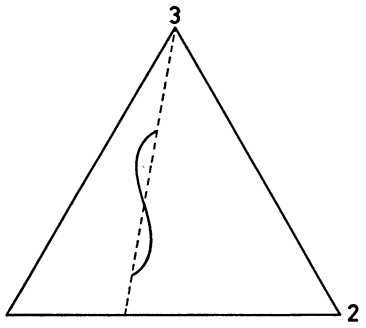

Fig. 1. Schematic diagram of diffusion path for ternary diffusion.

In a ternary diffusion given by Eqs. (8), a linear combination of two of the three concentrations given by Eq. (11) obeys Fick's law as is given by Eq. (12), in which the diffusion coefficient is $1/\mu^2$.

$$C = rC_2 + sC_1 \tag{11}$$

$$\frac{\partial C}{\partial t} = \frac{1}{\mu^2}\frac{\partial^2 C}{\partial x^2} \tag{12}$$

The μ and the ratio of r and s are defined as follows:

$$\mu_1 = \left\{\frac{D_1+D_2+N_1\,{}_3D_1+N_2\,{}_3D_2+[{}_2D_1{}^2+2_2D_1(N_2\,{}_3D_2-N_1\,{}_3D_1)+(N_1\,{}_3D_1+N_2\,{}_3D_2)^2]^{1/2}}{2(D_1D_2+N_1D_2\,{}_3D_1+N_2D_1\,{}_3D_2)}\right\}^{1/2},$$
$$\mu_2 = \left\{\frac{D_1+D_2+N_1\,{}_3D_1+N_2\,{}_3D_2-[{}_2D_1{}^2+2_2D_1(N_2\,{}_3D_2-N_1\,{}_3D_1)+(N_1\,{}_3D_1+N_2\,{}_3D_2)^2]^{1/2}}{2(D_1D_2+N_1D_2\,{}_3D_1+N_2D_1\,{}_3D_2)}\right\}^{1/2}, \tag{13}$$

$$R_1 = 1/S_1 = (r/s)_1 = \frac{{}_2D_1-N_1\,{}_3D_1+N_2\,{}_3D_2-[{}_2D_1{}^2+2_2D_1(N_2\,{}_3D_2-N_1\,{}_3D_1)+(N_1\,{}_3D_1+N_2\,{}_3D_2)^2]^{1/2}}{2N_2\,{}_3D_1},$$
$$R_2 = 1/S_2 = (r/s)_2 = \frac{{}_2D_1-N_1\,{}_3D_1+N_2\,{}_3D_2+[{}_2D_1{}^2+2_2D_1(N_2\,{}_3D_2-N_1\,{}_3D_1)+(N_1\,{}_3D_1+N_2\,{}_3D_2)^2]^{1/2}}{2N_2\,{}_3D_1}, \tag{14}$$

where ${}_iD_j=D_i-D_j$,
D is the intrinsic diffusion coefficient regarded as equal to the self-diffusion coefficient, N is the mole fraction, and subscript numbers refer to components.

B. Diaphragm-Cell Diffusion of Ternary System. When diffusion takes place through a diaphragm between two well-stirred cells, the concentration difference between the two cells varying with time is given by

$$\Delta c' = \Delta c \exp(-DKt) \tag{15}$$

where Δc is the concentration difference between two cells at time zero, $\Delta c'$ that at time t, D the diffusion coefficient, and K the cell constant.[6]

Similarly for a diaphragm-cell diffusion in a ternary system, the difference of linear combinations of the two concentrations between two cells is given by

$$\Delta C' = \Delta C \exp\left(-\frac{Kt}{\mu^2}\right) \tag{16}$$

where ΔC is the difference of linear combinations of two concentrations between two cells at time zero and $\Delta C'$ is that at time t, which are given by the following equations derived respectively from Eq. (11).

$$\Delta C = r\Delta C_2 + s\Delta C_1, \tag{17}$$

$$\Delta C' = r\Delta C_2' + s\Delta C_1', \tag{18}$$

where ΔC_i and $\Delta C_i'$ are the concentration differences of component i between two cells at times zero and t, respectively. It should be noted that Eq. (16) is quadratic, since μ and r/s are given in two pairs as in Eqs. (13) and Eqs. (14). Substituting Eqs. (17) and (18) in Eq. (16) we obtain

$$\left(\frac{r}{s}\right)_1\Delta C_2' + \Delta C_1' = \left[\left(\frac{r}{s}\right)_1\Delta C_2+\Delta C_1\right]\exp\left(-\frac{Kt}{\mu_1{}^2}\right) \tag{19a}$$

$$\left(\frac{r}{s}\right)_2\Delta C_2' + \Delta C_1' = \left[\left(\frac{r}{s}\right)_2\Delta C_2+\Delta C_1\right]\exp\left(-\frac{Kt}{\mu_2{}^2}\right) \tag{19b}$$

By solving the simultaneous equations for $\Delta C_1'$ and $\Delta C_2'$, we obtain the following equations.

$$\Delta C_1' = \frac{(\Delta C_2+S_1\Delta C_1)\exp\left(-\frac{Kt}{\mu_1{}^2}\right)-(\Delta C_2+S_2\Delta C_1)\exp\left(-\frac{Kt}{\mu_2{}^2}\right)}{S_1-S_2} \tag{20a}$$

5) Y. Oishi, *J. Chem. Phys.*, **43**, 1611 (1965).
6) J. H. Northrop and M. L. Anson, *J. Gen. Physiol.*, **12**, 543 (1929).

$$\Delta C_2' = \frac{(R_1\Delta C_2+\Delta C_1)\exp\left(-\frac{Kt}{\mu_1^2}\right)-(R_2\Delta C_2+\Delta C_1)\exp\left(-\frac{Kt}{\mu_2^2}\right)}{R_1-R_2} \tag{20b}$$

where

$$R_1=\frac{1}{S_1}=\left(\frac{r}{s}\right)_1, \qquad R_2=\frac{1}{S_2}=\left(\frac{r}{s}\right)_2.$$

Eqs. (20a) and (20b) give the differential concentrations between two cells for two of three components varying with time for the diaphragm-cell diffusion of a ternary system. The concentrations of the three components in the two cells are given by combining Eqs. (20a) and (20b) with the conditions of mass conservation for the respective components as follows.

$$C'_{1a}=\frac{\alpha C_{1a}+C_{1b}+\Delta C_1'}{1+\alpha} \tag{21a}$$

$$C'_{2a}=\frac{\alpha C_{2a}+C_{2b}+\Delta C_2'}{1+\alpha} \tag{21b}$$

$$C'_{3a}=(C_{1a}+C_{2a}+C_{3a})-(C'_{1a}+C'_{2a}) \tag{21c}$$

$$C'_{1b}=\frac{\alpha C_{1a}+C_{1b}-\alpha\Delta C_1'}{1+\alpha} \tag{22a}$$

$$C'_{2b}=\frac{\alpha C_{2a}+C_{2b}-\alpha\Delta C_2'}{1+\alpha} \tag{22b}$$

$$C'_{3b}=(C_{1b}+C_{2b}+C_{3b})-(C'_{1b}+C'_{2b}) \tag{22c}$$

where C_{ia} and C_{ib} are the initial concentrations of component i in cell a and cell b, respectively, C_{ia}' and C_{ib}' the concentrations of component i at time t in cell a and cell b, respectively, and α the ratio of the volumes of cell a and cell b. The concentrations of the three components in the two cells can be calculated for an arbitrary time by using Eqs. (21a), (21b), (21c), (22a), (22b), and (22c).

Experimental

Apparatus. Experiments were carried out by means of the diaphragm-cell technique of Ney-Armistead type[7] (Fig. 2). Cell 1 is movable along the ground glass plate relative to cell 2. Balance of pressures of cells 1 and 2 was ascertained by using an oil-manometer. Pressure was measured with a mercury manometer. The cell constant of the apparatus, K, was determined by using the self-diffusion coefficient of carbon dioxide by Winn[8] as a standard.

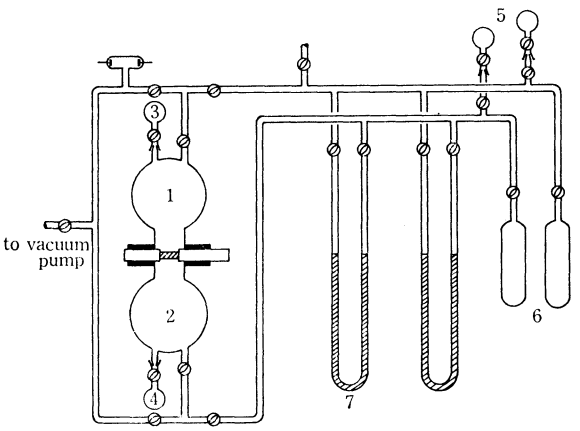

Fig. 2. Diffusion Apparatus:
1: upper cell, 2: lower cell, 3: upper sample holder, 4: lower sample holder, 5: sample holder, 6: gas holder, and 7: manometer.

Samples. Commercial neon gas of 99.99% purity (Mathison Co., U.S.A.) and commercial carbon dioxide gas of 99.95% purity (Nihon Tansan, Japan) were used without further purification. The isotope ratios of these gases are of natural abundance ratios. CO_2 gas was ^{18}O-enriched with the use of exchange reaction between $C^{16}O^{16}O$ and ^{18}O-enriched oxygen of 5% enrichment on the surface of a red-heated iron wire. The ^{18}O-enriched oxygen gas was obtained from commercial ^{18}O-enriched water by electrolysis.

Procedures. For measurement of the cell constant, the ^{18}O-enriched CO_2 gas was placed in cell 2 and natural CO_2 gas in cell 1 with the diffusion path between the two cells shut off by a glass plate. After the pressure of cell 1 was balanced to that of cell 2, cell 1 was shifted relative to cell 2 to open the diffusion path through the glass filter. A similar procedure was taken for the measurements of self-diffusion coefficients of CO_2 in a binary mixture of Ne and CO_2. All the experiments were carried out at 25°C under 760 mmHg. The diffusion apparatus was set in a vinyl sheet case installed in a temperature controlled room within 25±0.5°C. The diffusion time was about 100 minutes so that the ratio of M_t/M_∞ came up to one third. M_t and M_∞ stand for the amounts of diffusion at time t and infinity, respectively.

The composition of binary mixture of Ne–CO_2 system and the isotope ratio of ^{20}Ne and ^{22}Ne were determined by a mass spectrometer (Hitachi RM-60R). Accurate measurement of the isotope ratio of ^{20}Ne and ^{22}Ne in the mixture of Ne and CO_2 gases is disturbed by the coexisting CO_2, since the mass spectrometer does not distinguish $^{22}Ne^+$ ion from $^{44}CO_2^{2+}$ ion. To get rid of the disturbance it was necessary to remove CO_2 from the gas mixture with a cold trap of liquid nitrogen.

Results

The self-diffusion coefficients[9] of CO_2 for the binary system of Ne and CO_2 were measured for various compositions. The results are summarized in Table 1. The reciprocals of the self-diffusion coefficients of CO_2 are plotted in Fig. 3 as a function of the mole fraction of CO_2.

The variation of the isotope ratio of $^{22}Ne/^{20}Ne$ during interdiffusion of Ne and CO_2 was examined by considering the system as a ternary system of ^{22}Ne, ^{20}Ne, and $^{44}CO_2$. The results are given in Table 2 and plotted in Fig. 4, where M_t and M_∞ stand for the amounts of Ne diffusing into the CO_2 cell after time t, and infinite time, respectively, and R_i and R_t are the $^{22}Ne/^{20}Ne$ ratios at times zero and t, respectively. In Fig. 4 the circles show experimental results and the

7) E. P. Ney and F. C. Armistead, *Phys. Rev.*, **71**, 14 (1947).

8) E. B. Winn, *ibid.*, **80**, 1024 (1950).

9) "Self-diffusion coefficient" referred to in this paper is defined as the diffusion coefficient for diffusion in a homogeneous system where no chemical concentration gradient exists. The term is used for the diffusion coefficient not only in a pure system of a single component but also in a homogeneous multicomponent system. Thus, the intradiffusion coefficient defined by Albright and Mills (*J. Phys. Chem.*, **69**, 3120 (1965)) and McCarty and Mason (*Phys. Fluids*, **3**, 908 (1960)) is included in the definition of self-diffusion coefficient given above.

Table 1. Self-diffusion coefficient of CO_2 in the system of Ne and CO_2 at 25°C and 760 mmHg

Mole fraction of CO_2	D (cm²/sec)
1.000	0.113
0.796	0.123
0.624	0.131
0.500	0.137
0.356	0.153
0.189	0.179

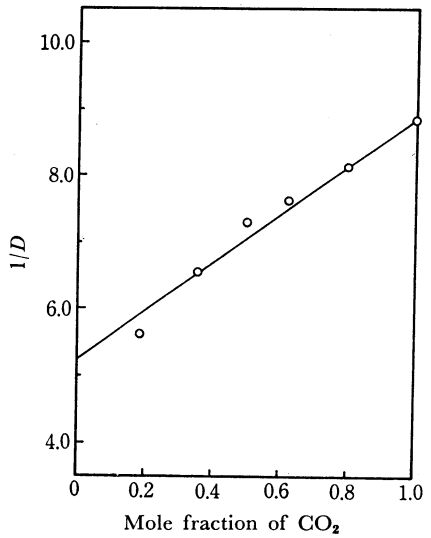

Fig. 3. Self-diffusion coefficient of CO_2 in the system of CO_2 and Ne at 25°C and 760 mmHg.

Table 2. Variation of isotope ratio $^{22}Ne/^{20}Ne$ during diffusion of a ternary system ^{20}Ne-^{22}Ne-CO_2 at 25°C and 760 mmHg

Diffusion time (min)	M_t/M_∞	$(R_t-R_i)/R_i$ Cell 1	$(R_t-R_i)/R_i$ Cell 2
20	0.225	4.83×10^{-3}	-4.15×10^{-2}
20	0.226	4.83	−3.47
30	0.292	6.80	−3.79
30	0.299	6.76	−3.57
45	0.450	10.61	−3.38
60	0.537	10.68	−3.01
75	0.619	9.65	−2.22
90	0.690	11.65	−2.14
90	0.704	12.62	−2.14
120	0.804	10.68	−1.55

soild lines represent the theoretical values calculated by Eqs. (20a) and (20b) with the values of the self-diffusion coefficients of ^{20}Ne,^{22}Ne, and $^{44}CO_2$.

For calculation of the theoretical values, the self-diffusion coefficients of the respective components for the composition of 0.5 mole fraction of CO_2 were taken as average values. The self-diffusion coefficients of ^{20}Ne for the composition of 0.5 mole fraction of CO_2 was estimated by making use of Darken's relation

$$D = N_2D_1^* + N_1D_2^*$$

where D denotes the binary diffusion coefficient of

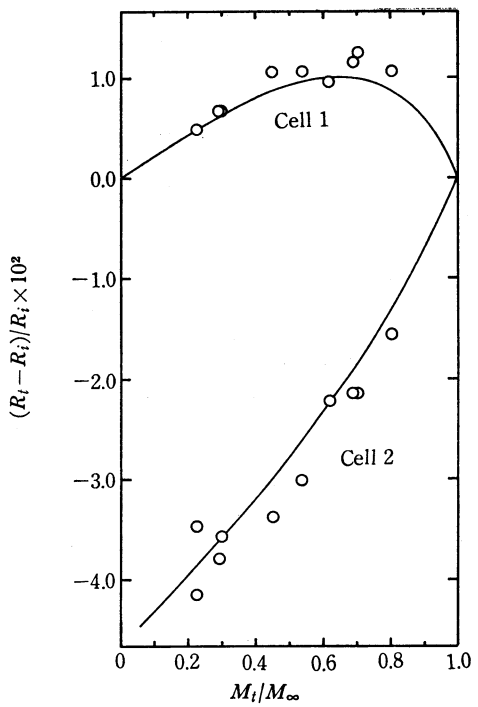

Fig. 4. Variation of isotope ratio $^{22}Ne/^{20}Ne$ during diffusion of a ternary system ^{20}Ne-^{22}Ne-CO_2 at 25°C and 760 mmHg.

the system of Ne and CO_2, D_1^* and D_2^* repersent the self-diffusion coefficients of Ne and CO_2, and N_1 and N_2 mole fractions of the components, respectively. Thus the self-diffusion coefficient of ^{20}Ne can be calculated since we have measured the self-diffusion coefficient of CO_2 and the interdiffusion coefficient of the binary system are known.[10] Estimation of the self-diffusion coefficient of ^{22}Ne was made by means of the mass correction

$$D(^{22}Ne) = \left(\frac{M_2+M_1}{M_2+M_3}\times\frac{M_3}{M_1}\right)^{1/2} D(^{20}Ne) \qquad (23)$$

where $D(^{22}Ne)$ denotes the self-diffusion coefficient of ^{22}Ne in the binary system of ^{22}Ne and $^{44}CO_2$, $D(^{20}Ne)$ the self-diffusion coefficient of ^{20}Ne in the binary system of ^{20}Ne and $^{44}CO_2$, and M_1,M_2, and M_3, the masses of ^{22}Ne, $^{44}CO_2$, and ^{20}Ne, respectively.

Discussion

A. Self-diffusion Coefficients. A kinetic theory gives the following relations between three kinds of diffusion coefficients:

$$\frac{1}{D_1^*} = \frac{N_1}{D_{11}} + \frac{N_2}{D_{12}}$$
$$\frac{1}{D_2^*} = \frac{N_2}{D_{22}} + \frac{N_1}{D_{12}} \qquad (24)$$

where D_1^* and D_2^* denote self-diffusion coefficients of species 1 and 2 for a binary mixture, D_{11} and D_{22} self-diffusion coefficients for the respective pure system, D_{12} an interdiffusion coefficient for the binary system,

10) B. K. Annis, A. E. Humphreys, and E. A. Mason, *Phys. Fluids*, **12**, 78 (1969).

and N_1 and N_2 mole fractions of the respective components. The equations show that the reciprocal of the self-diffusion coefficient of one component in a binary system are dependent linearly upon its mole fraction if the interdiffusion coefficient is independent of composition. The experimental results for CO_2 support the relation (Fig. 3). The data for the smaller mole fractions of CO_2 deviate from the straight line. This is probably due to the experimental error tending to be larger than that for the larger mole fraction of CO_2 because of the fact that the CO_2 content in the binary system is insufficient for accurate measurement of isotope ratios of $C^{16}O^{18}O/C^{16}O^{16}O$.

B. Isotope Separation in Ternary Diffusion. The agreement of the theoretically calculated variation of the isotope ratio $(R_t-R_i)/R_i$ with the experimental results indicates the validity of Eqs. (8).

Consequence of Eqs. (8), (20a), and (20b) with respect to the present isotope separation of neon shows that the greater the difference of self-diffusion coefficients of ^{22}Ne and ^{20}Ne, the higher the degree of isotope separation of neon, and that the smaller the self-diffusion coefficient of CO_2 that those of ^{22}Ne and ^{20}Ne, the greater the mass flow toward the neon side and the higher the degree of isotope separation of neon.

Kinetic theory predicts the mass dependency of the ratio of the self-diffusion coefficients:

$$\frac{D_1^*}{D_2^*} \propto \frac{(1/M_1+1/M_3)^{1/2}}{(1/M_2+1/M_3)^{1/2}} = \left(\frac{M_2}{M_1} \times \frac{1+M_1/M_3}{1+M_2/M_3}\right)^{1/2} \quad (25)$$

where M_i is the mass of i species.

Therefore, when M_3 is much larger than M_1 and M_2, the D_1^*/D_2^* ratio tends to approach the maximum value $(M_2/M_1)^{1/2}$, if M_2 is greater than M_1. Moreover, the large mass of the third component relative to ^{20}Ne and ^{22}Ne gives rise to its small self-diffusion coefficient and subsequently to the large mass flow, which is more effective for the purpose of the isotope separation of ^{20}Ne from ^{22}Ne. Consequently the larger separation factor can be obtained when the mass of the third component is larger than that of CO_2.