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Relationship between Self-Diffusion and Interdiffusion in Gaseous Systems

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Self-diffusion coefficients of oxygen and interdiffusion coefficients were measured for the O_2–He system at 25 °C under 760 Torr. The interdiffusion coefficients obtained were compared with theoretical values calculated by the kinetic theory and by Darken's phenomenological theory. The phenomenological equation was tested in comparison with the kinetic theory by making use of the results and the data reported by other investigators. A criterion determining the magnitude or error of the phenomenological equation was given.

The interrelation between self-diffusion[1] and interdiffusion coefficients for gaseous systems has been described by rigorous kinetic theory. However, calculation has been successful only for dilute gaseous systems, the kinetic theory failing to describe satisfactorily the interdiffusion for condensed systems in terms of self-diffusion coefficients. So far the data of interdiffusion have been analyzed only by means of the phenomenological equation. Darken[2] introduced the concept of intrinsic diffusion flux density for the respective components to explain the Kirkendall effect observed in the interdiffusion of a metallic alloy system and derived a phenomenological equation. This has been widely applied in the analysis of interdiffusion in binary metallic systems. Essentially the same equation was also derived by Hartley and Crank[3] and tested by many

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[1] "Self-diffusion coefficient" 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 single component but also in a homogeneous multicomponent system. Thus, the effective diffusion coefficient defined by the kinetic theory and the intradiffusion coefficient defined by Albright and Mills (*J. Phys. Chem.*, **69**, 3120 (1965)) and McCarty and Mason (*Phys. Fluids*, **3**, 908 (1960)) are included in the present definition.

[2] L. S. Darken, *Trans. AIME*, **175**, 184 (1948).

[3] G. S. Hartley and J. Crank, *Trans. Faraday Soc.*, **45**, 801 (1949).

authors for various organic binary solutions. The simple form of Darken's equation has the advantage that it can be easily extended to diffusion in the systems of more than two components. An extension to the ternary system has been made for a Ne^{20}–Ne^{22}–CO_2 system with satisfactory results.[4] The Kirkendall effect has also been observed in the interdiffusion in gaseous systems.[5] In Darken's equation the diffusion flux density relative to the external frame is given as a sum of the intrinsic diffusion flux density and the mass flow term. The intrinsic diffusion coefficients are assumed to be equal to the self-diffusion coefficients for the ideal systems, and the interdiffusion coefficient is given by

$$D_{\mathrm{AB}} = N_{\mathrm{B}}D_{\mathrm{A}}^* + N_{\mathrm{A}}D_{\mathrm{B}}^* \tag{1}$$

where D_{AB} is the interdiffusion coefficient, N mole fraction, D^* the self-diffusion coefficients, and subscripts A and B refer to components A and B, respectively.

McCarty and Mason[6] and Miller and Carman[7] examined the validity of Darken's equation for the interdiffusion in gaseous systems and found that Eq. (1) was less accurate than the following equation derived from the kinetic theory.

$$\frac{1}{D_{\mathrm{A}}^*} = \frac{N_{\mathrm{A}}}{D_{\mathrm{A^*A}}} + \frac{N_{\mathrm{B}}}{D_{\mathrm{AB}}} \tag{2}$$

McCarty and Mason further pointed out that Eq. (1) is consistent with Eq. (2) only in the case

$$\frac{D_{\mathrm{AB}}^2}{D_{\mathrm{A^*A}}D_{\mathrm{B^*B}}} = 1. \tag{3}$$

Deviation of the ratio from unity can be a measure for the error resulting from application of the phenomenological equation to a gaseous system for which the kinetic theory holds.

In the present paper, the criterion by means of $D^2{}_{\mathrm{AB}}/D_{\mathrm{A^*A}}D_{\mathrm{B^*B}}$ has been transformed into mass and potential terms. Thus the magnitude of a possible error coming from the phenomenological equation when applied to an actual system can be estimated with thermodynamic data without knowing the self-diffusion and interdiffusion coefficients. The derived criterion was tested with various binary systems. Necessary self-diffusion coefficients and interdiffusion coefficients were measured by a conventional diaphragm-cell method.

Experimental

Experiments were carried out by means of a Ney-Armistead type[8] diaphragm-cell technique. The cell constant was determined by using the self-diffusion coefficient of carbon dioxide determined by Winn[9] as a standard. The details of the apparatus have been described elsewhere[4].

Commercial helium gas and oxygen gas both of 99.99% purity (Osaka Sanso Co., Japan) were used without further purification. The isotope ratios of these gases were of natural abundance. The O^{18}-enriched oxygen gas was obtained from O^{18}-enriched water by electrolysis. CO_2 gas was O^{18}-enriched with the use of exchange reaction between $CO^{16}O^{16}$ and 5% O^{18}-enriched oxygen on the surface of a red-hot iron wire. Gas mixtures of O_2 and He having the required compositions were prepared in separate storage vessels, transferred into the diffusion cells by means of a Toepler pump, and a diffusion run was then performed. In the measurements of self-diffusion coefficients of O_2 in binary mixtures of O_2 and He, both sides of the diffusion couple were made to have the same chemical composition and one side enriched with O^{18}. For measurements of interdiffusion coefficients the composition difference between the diffusion couple was taken to be approximately 0.2 mole fraction of He. In all experiments the denser gas mixture was placed in the lower cell. Measurements were carried out at 25±0.5 °C under 760 Torr.

The compositions of the binary mixtures of O_2 and He and the isotope ratios of $^{16}O_2$ and $^{17}O_2$ were determined with a mass spectrometer.

Results

Self-diffusion coefficients of O_2 in the binary system of O_2 and He were measured for several compositions. The results are summarized in Table 1. Interdiffusion coefficients for the binary system of O_2 and He were also measured for three compositions. The results are summarized in Table 2. The reciprocals of these diffusion coefficients are plotted as a function of the mole fraction of He in Fig. 1. Equation (2) shows that the reciprocal of the self-diffusion coefficient of one component in a binary system is dependent linearly upon its mole fraction, if the interdiffusion coefficient is independent of composition. The relation holds in the results for O_2 (Fig. 1). The self-diffusion coefficients of He in the binary system of O_2 and He (chain line) were estimated from Eq. (2) by using the value of the self-diffusion coefficient of He in the pure He system $D_{\mathrm{B^*B}}$,[10] where the self-diffusion coefficient of He for

TABLE 1. SELF-DIFFUSION COEFFICIENTS OF O_2 FOR THE O_2–He BINARY SYSTEMS

Mole fraction of He	D_{A}^*
0.000	0.199
0.201	0.236
0.444	0.304
0.606	0.359
0.750	0.443
0.900	0.547

TABLE 2. INTERDIFFUSION COEFFICIENTS FOR THE O_2–He SYSTEM

Mole fraction of He	D_{AB}
0.504	0.682
0.696	0.747
0.898	0.778

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[4] Y. Oishi, M. Sugisaki, Y. Kamei, and Y. Shono, This Bulletin, **45**, 2984 (1972).

[5] 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).

[6] K. P. McCarty and E. A. Mason, *ibid.*, **3**, 908 (1960).

[7] L. Miller and P. C. Carman, *Trans. Faraday Soc.*, **57**, 2143 (1961).

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

[9] E. B. Winn, *ibid.*, **80**, 1024 (1950).

[10] The value extrapolated for 25 °C from the data by P. J. Bendt, *Phys. Rev.*, **110**, 85 (1958).

TABLE 3. COMPARISON OF $(m_A+m_B)/2\sqrt{m_A m_B}$ WITH THE EXPERIMENTAL VALUE $(D_{AB})^2/(D_{AA}D_{BB})$

A	B	T[°C]	D_{AB}	D_{AA}	D_{BB}	$(D_{AB})^2/(D_{AA}D_{BB})$	Ω	$(m_A+m_B)/2\sqrt{m_A m_B}$
He	— N_2	25	0.687[a]	1.57[f]	0.212[h]	1.42	0.931	1.51
He	— O_2	25	0.729[a]	1.57[f]	0.232[h]	1.46	1.00	1.59
					(0.202)[j]	(1.68)		
He	— Ar	25	0.729[a]	1.57[f]	0.178[h]	1.90	1.03	1.74
He	— CO_2	25	0.612[a]	1.57[f]	0.113[h]	2.11	0.994	1.81
H_2	— N_2	0	0.674[b]	1.29[b]	0.185[h]	1.90	0.967	2.00
H_2	— CH_4	0	0.625[b]	1.29[b]	0.206[h]	1.47	1.03	1.59
H_2	— O_2	0	0.697[b]	1.29[b]	0.187[h]	2.01	0.999	2.12
H_2	— CO	0	0.651[b]	1.29[b]	0.190[g]	1.73	0.962	2.00
H_2	— CO_2	0	0.550[b]	1.29[b]	0.0970[i]	2.42	1.01	2.44
CO	— O_2	0	0.185[c]	0.190[g]	0.187[h]	0.96	0.999	1.00
CO	— N_2	0	0.192[b]	0.190[g]	0.185[h]	1.05	1.00	1.00
CO	— CO_2	0	0.137[b]	0.190[g]	0.0970[i]	1.02	1.07	1.03
CO	— Ne	25	0.259[d]	0.113[h]	0.516[h]	1.15	0.980	1.08
CO_2	— N_2	25	0.158[c]	0.113[h]	0.212[h]	1.04	1.04	1.03
CO_2	— CH_4	0	0.153[b]	0.0970[i]	0.206[h]	1.17	0.998	1.13
N_2	— O_2	0	0.181[c]	0.185[h]	0.187[h]	0.95	0.999	1.00
Xe	— Ar	0	0.0962[e]	0.0480[e]	0.156[h]	1.24	0.977	1.18

$$\Omega=\frac{\sigma_{AA}{}^2W_{AA}{}^{(1)}\ \sigma_{BB}{}^2W_{BB}{}^{(1)}}{(\sigma_{AB}{}^2W_{AB}{}^{(1)})^2}$$

a) S. L. Seager, L. R. Geertson, and J. C. Giddings, *J. Chem. Eng. Data*, **8**, 168 (1963).
b) "American Institute of Physics Handbook" (1957).
c) N. H. Chen and D. F. Othmer, *J. Chem. Eng. Data*, **7**, 37 (1962).
d) J. D. Breetveld, R. DiPippo, and J. Kestine, *J. Chem. Phys.*, **45**, 124 (1966); from mixture viscosity.
e) I. Amdure and T. F. Schatzki, *J. Chem. Phys.*, **27**, 1049 (1957).
f) The value extrapolated for 25 °C from the data by P. J. Bendt, *Phys. Rev.*, **110**, 85 (1958).
g) S. Weissman, *J. Chem. Phys.*, **40**, 3397 (1964).
h) E. B. Winn, *Phys. Rev.*, **80**, 1024 (1950).
i) I. Amdure, J. W. Irvine, Jr., E. A. Mason, and J. Ross, *J. Chem. Phys.*, **20**, 436 (1952).
j) Present experimental result.

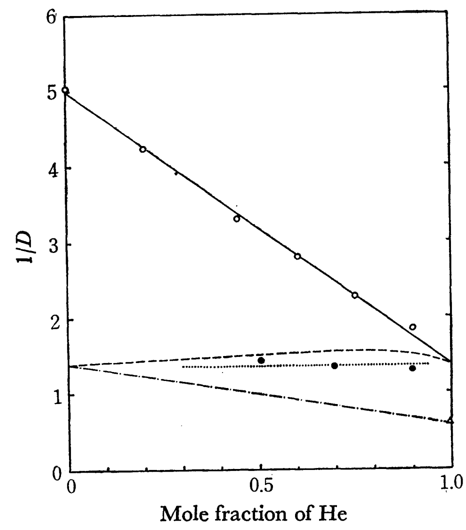

Fig. 1. Reciprocal of diffusion coefficients for the O_2–He system; ○, experimental self-diffusion coefficients of O_2; ●, experimental interdiffusion coefficients; -·-·-, estimated self-diffusion coefficients of He; △, experimental value by Bendt[9]; ------, theoretical interdiffusion coefficients by the phenomenological equation; ······, theoretical interdiffusion coefficients by the kinetic theory.

zero mole fraction of He should be equal to the interdiffusion coefficient for the same composition.

The value of the interdiffusion coefficient D_{AB} calculated by Eq. (2) is 0.721, which agrees closely with the average of our values, 0.736. Seager *et al.*[11] and Wasik *et al.*[12] also reported the values, 0.729, 0.736, respectively. The interdiffusion coefficients for the O_2–He system were calculated by the kinetic theory for cases in which the various data[13] of potential parameters were available. The calculation gives a maximum 0.751 and minimum 0.708. The average value, shown in Fig. 1 by a dotted line, agrees well with the experimental results. For the sake of comparison, the results obtained by Eq. (1) are also shown (broken line), maximum deviation from experimental result being approximately 14.7%. This deviation should be attributed to the approximation made in the derivation of Darken's equation.

Discussion

A Criterion for Comparison of the Phenomenological Equation with the Kinetic Theory. For the case where the rigorous kinetic theory is valid, the applicability of Eq. (1) can be tested by whether the ratio $D^2{}_{AB}/$

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[11] S. L. Seager, L. R. Geertson, and J. C. Giddings, *J. Chem. Eng. Data*, **8**, 168 (1963).

[12] S. P. Wasik and K. E. McCulloh, *J. Res. Nat. Bur. Std.*, **73A**(2), 207 (1969).

[13] The potential parameters were obtained according to the combining rule from the force constants data determined by viscosity and 2nd virial coefficients measurements at various temperatures (see also Ref. (15)).

$(D_{\mathrm{A^*A}} D_{\mathrm{B^*B}})$ is unity or not, as mentioned by McCarty and Mason. For the O_2–He system at 25 °C, we obtain

$$\frac{D_{\mathrm{AB}}^2}{D_{\mathrm{A^*A}} D_{\mathrm{B^*B}}} = \frac{(0.729)^2}{(0.199)(1.69)} = 1.57$$

The deviation from unity may be taken as a measure for the deviation of the interdiffusion coefficient obtained by the phenomenological equation from the correct value, the square root of 1.57 indicating the deviation.

This criterion can be further simplified and rewritten by use of the rigorous kinetic theory. In order to simplify the derivation, we let $D_{\mathrm{A^*A}}$ and $D_{\mathrm{B^*B}}$ equal to D_{AA} and D_{BB} respectively. The interdiffusion coefficient D_{ij} is then expressed as follows:[14]

$$D_{ij} = 0.00092916 \frac{T^{3/2}\sqrt{(m_i + m_j)/m_i m_j}}{P\sigma_{ij}^2 W_{ij}^{(1)}(1 : \varepsilon_{ij}/kT)} \ [\mathrm{cm^2/s}] \qquad (4)$$

where P is pressure [atm], T temperature [K], σ_{ij} and ε_{ij} the potential parameters, m_i and m_j molecular masses, and $W_{ij}{}^{(1)}$ $(1 : \varepsilon_{ij}/kT)$ the term associated with the collision integral. Thus, we obtain

$$\frac{D_{\mathrm{AB}}^2}{D_{\mathrm{AA}} D_{\mathrm{BB}}} = \frac{(m_{\mathrm{A}} + m_{\mathrm{B}})}{2\sqrt{m_{\mathrm{A}} m_{\mathrm{B}}}} \left[\frac{\sigma_{\mathrm{AA}}^2 W_{\mathrm{AA}}^{(1)} \sigma_{\mathrm{BB}}^2 W_{\mathrm{BB}}^{(1)}}{(\sigma_{\mathrm{AB}}^2 W_{\mathrm{AB}}^{(1)})^2} \right] \qquad (5)$$

Values of $D^2{}_{\mathrm{AB}}/D_{\mathrm{AA}} D_{\mathrm{BB}}$ for various systems were calculated by use of experimental data and compared with $(m_{\mathrm{A}} + m_{\mathrm{B}})/2\sqrt{m_{\mathrm{A}} m_{\mathrm{B}}}$. Some of the examples are listed in Table 3. It is noted that the values of Ω,[15] *i.e.* the term in the brackets in Eq. (5) are close to unity, so $D^2{}_{\mathrm{AB}}/D_{\mathrm{AA}} D_{\mathrm{BB}}$ may be approximated to $(m_{\mathrm{A}} + m_{\mathrm{B}})/2\sqrt{m_{\mathrm{A}} m_{\mathrm{B}}}$, if a few percent error is allowed. Thus the discrepancy of the phenomenloogical equation from Eq. (2) is ascribed mostly to the deviation of $(m_{\mathrm{A}} + m_{\mathrm{B}})/2\sqrt{m_{\mathrm{A}} m_{\mathrm{B}}}$ from unity.

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[14] J. O. Hirschfelder, R. B. Bird, and E. L. Spotz, *Chem. Rev.*, **44**, 205 (1949); *J. Chem. Phys.*, **16**, 968 (1948).

[15] The values of Ω were calculated for various systems on the basis of the Lennard-Jones (12: 6) potential model by means of a computer. The potential parameters σ_{ij} and ε_{ij} in all combinations were calculated according to the combining rules:

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj})$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii} \cdot \varepsilon_{jj}}$$

from the force constants listed in the Appendix of "Molecular Theory of Gases and Liquids" (J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, John Willy & Sons, Inc., New York, 1964).