Binary Diffusion Coefficients of Low-Density Gases
II. Molecular Parameters and Combining Rules

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Lennard-Jones (12-6) parameters are evaluated for 23 gas pairs from the binary diffusion data given in Part I. Stockmayer parameters are determined for one additional pair, CH_3Cl-C_2H_5Cl. The data for hydrogen and paraffins are fitted with a relative standard deviation of 0.0045 when both σ_{AB} and ϵ_{AB} are adjusted, vs. 0.016 when either σ_{AB} or ϵ_{AB} is predicted from viscosities of pure *A* and *B*, and 0.041 when both σ_{AB} and ϵ_{AB} are thus predicted. The arithmetic-mean rule for predicting σ_{AB} is distinctly better than the geometric mean. Corresponding states methods for prediction of σ_{AB} and ϵ_{AB} from pure fluid properties are tested.

Diffusion measurements in gases at low density can provide useful information about forces between unlike molecules, particularly if the measurements cover a range of temperature (*3, 4*). The information obtained is generally model dependent—the results are specific to the model of intermolecular forces that one assumes. Here, we analyze the data of Part I [Gotoh et al. (*2*)] to obtain collision parameters for 24 molecular pairs. The Lennard-Jones (12-6) and Stockmayer (12-6-3) potentials are used for computational convenience.

Theory

The kinetic theory of gases provides the following expression for D_{AB} at low densities:

$$cD_{AB} = 2.2646 \times 10^{-5} \frac{\sqrt{T(1/M_A + 1/M_B)}}{\sigma_{AB}^2 \Omega^{(1,1)*}(kT/\epsilon_{AB})} f_D^{(2)} \quad (1)$$

The details of the collision dynamics are contained in the functions $\Omega^{(1,1)*}$ (kT/ϵ_{AB}) and $f_D^{(2)}$. (For the Stockmayer potential, $\Omega^{(1,1)*}$ depends on a reduced dipole moment $\delta_{\max}$, in addition to kT/ϵ_{AB}). We use the tables of Monchick and Mason (*6*) to calculate the needed collision integrals, and we use Mason's Kihara-type expansion (5) for $f_D^{(2)}$.

Experiments on self-diffusion (*10*) have indicated that Equation 1 is accurate nearly up to the critical density, provided that the true molar density *c* (rather than p/RT) is used. The calculation of *c* was done with two terms of the virial equation with the compressibility parameters given in Part I. For our experiments, the reciprocal compressibility factors cRT/p ranged from 1.0 to 1.03; this is comparable to the range of the correction factors $f_D^{(2)}$.

Calculations

Calculations were made to compare various methods of determining σ_{AB} and ϵ_{AB} in Equation 1. The results for hydrogen and paraffins are shown in Table I. Models 1 and 2 use constants determined from viscosity of the pure components; Models 3-5 include constants fitted to the diffusion data for each gas pair; Model 6 uses pure-component constants fitted to all the diffusion data. Models 7-12 use pure-component constants constrained by corresponding states relations of the form:

$$(p_c/T_c)_i^{1/3}\sigma_i = a_1 \exp(b_1\omega_i) \quad (2)$$

$$(\epsilon/kT_c)_i = a_2 \exp(b_2\omega_i) \quad (3)$$

for the paraffins. Expressions of this type were previously used by Tee et al. (*8*) to represent other properties of normal fluids. The constants for Models 6-12 are given in Tables 3-5 (deposited with the ACS Microfilm Depository Service), along with the individual deviations for several models.

Table II shows the fitted constants for each gas pair, determined as in Models 3-5 of Table I. The standard deviation and the confidence intervals of the fitted parameters are included.

The diffusivity data used here are the same as in Part I, except for the omission of two tests: CH_4-SF_6 at 297.6K and CH_3Cl-C_2H_5Cl at 378.2K. These tests were deleted because of deviations from the overall trend of results for these two gas pairs.

The factor $f_D^{(2)}$ was calculated in all cases from the viscosity parameters given in Part I. The parameters σ_{AB} and ϵ_{AB} for this calculation were obtained as in Model 1, except for Models 2, 8, and 10 where the combining rules of Model 2 were used.

Discussion of Results (Hydrogen and Paraffins)

Model 1, Table I is the usual method of calculation of D_{AB}, based on viscosities of pure *A* and *B*, as described by Hirschfelder et al. (*3*). It predicts D_{AB} with a standard deviation of 4.1% (s = 0.041). The mean deviation (−0.67%) is smaller than comparisons with previous data have shown (*7, 9*). The individual deviations are shown in Part I and are somewhat systematic.

Model 2 differs from Model 1 in taking $\sigma_{AB} = \sqrt{\sigma_A\sigma_B}$, rather than $\sigma_{AB} = (\sigma_A + \sigma_B)/2$. This method of predicting σ_{AB} is less satisfactory; the standard deviation (s = 0.073) is nearly twice as large, and the calculated values tend to be too high. This conclusion is different from that reached by Good and Hope (*1*) from calculations of second virial coefficients, B_{AB}. The discrepancy may be due to the different dependence of D_{AB} and B_{AB} on the intermolecular potential, and to the approximate nature of the Lennard-Jones model.

Model 3 and 4 use one Lennard-Jones parameter predicted from viscosity and one fitted to the diffusion data. The accuracies are comparable (s = 0.0162 and 0.0165). Model 5 uses fitted values of both σ_{AB} and ϵ_{AB} and gives the most accurate fit obtainable with the Lennard-Jones model (s = 0.0045). The parameters found from Model 5 have larger uncertainties, as indicated in Table II, and three of the systems yielded no solution.

In Model 6 the Lennard-Jones parameters for each pure substance are determined from the diffusion data and combining rules. Within the accuracy shown (s = 0.026), this model may be regarded as an interpolation device for representing both D_{AB} (the binary diffusivity) and D_{AA} (the self-diffusivity) for these substances. The improvement in accuracy over Model 1 thus suggests differences between the Lennard-Jones parameters for viscosity and for self-diffusion.

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Table I. Comparison of Calculation Methods for D_{AB} in Paraffin and Hydrogen–Paraffin Systems

	Source of Molecular Parameters[a]								
Model	σ_{H_2}[b]	ϵ_{H_2}[b]	$\sigma_{i,i\neq H_2}$[b]	$\epsilon_{i,i\neq H_2}$[b]	σ_{AB}	ϵ_{AB}	N_p[c]	s[d]	Mean dev, %
1	Part I	Part I	Part I	Part I	$(\sigma_A+\sigma_B)/2$	$\sqrt{\epsilon_A\epsilon_B}$	0	0.041	−0.67
2	Part I	Part I	Part I	Part I	$\sqrt{\sigma_A\sigma_B}$	$\sqrt{\epsilon_A\epsilon_B}$	0	0.073	3.20
3	...	Part I	...	Part I	Fitted	$\sqrt{\epsilon_A\epsilon_B}$	20	0.0162	0.02
4	Part I	...	Part I	...	$(\sigma_A+\sigma_B)/2$	Fitted	20	0.0165	−0.05
5	...	...	...	...	Fitted	Fitted	34	0.0045[e]	0.00
6	Fitted	Fitted	Fitted	Fitted	$(\sigma_A+\sigma_B)/2$	$\sqrt{\epsilon_A\epsilon_B}$	14	0.026	0.03
7	Part I	Part I	(*8*, correl. iii)		$(\sigma_A+\sigma_B)/2$	$\sqrt{\epsilon_A\epsilon_B}$	0	0.044	0.25
8	Part I	Part I	(*8*, correl. iii)		$\sqrt{\sigma_A\sigma_B}$	$\sqrt{\epsilon_A\epsilon_B}$	0	0.080	3.58
9	Fitted	Part I	(*8*, correl. iii)		$(\sigma_A+\sigma_B)/2$	$\sqrt{\epsilon_A\epsilon_B}$	1	0.039	−0.88
10	Fitted	Part I	(*8*, correl. iii)		$\sqrt{\sigma_A\sigma_B}$	$\sqrt{\epsilon_A\epsilon_B}$	1	0.052	0.19
11	Fitted	Part I	Equations 2, 3: a_1, a_2 fitted; b_1, b_2 as in Model 7		$(\sigma_A+\sigma_B)/2$	$\sqrt{\epsilon_A\epsilon_B}$	3	0.038	0.17
12	Fitted	Part I	Equations 2, 3: a_1, a_2, b_1, b_2 fitted		$(\sigma_A+\sigma_B)/2$	$\sqrt{\epsilon_A\epsilon_B}$	5	0.029	0.04

[a] All "Fitted" values are derived from the diffusivity data for these systems (60 experiments). [b] For use when needed in prediction of σ_{AB} and ϵ_{AB}. [c] N_p is the number of parameters fitted to the diffusion data (60 experiments). [d] s is the standard deviation of ln $(D_{AB,\text{pred}}/D_{AB,\text{obsd}})$ based on $(60 - N_p)$ degrees of freedom. [e] Result for 17 systems fitted with this model (Table II).

Models 7 and 8 are similar to Models 1 and 2, except that Equations 2 and 3 are used for the paraffins. The constants a_1, a_2, b_1, b_2 are taken from Tee et al. (*8*). The accuracy compares well with Models 1 and 2, and the additive rule for σ_{AB} is again preferred.

Models 9 and 10 differ from Models 7 and 8 in using values of $\sigma_{H(2)}$ determined from the diffusion data. The predictions with the geometric rule for σ_{AB} are considerably improved (from 0.080 to 0.052), but the additive rule remains superior ($s = 0.039$).

Comparison of Model 6 ($s = 0.026$) with Model 9 ($s = 0.039$) indicates that Correlation (iii) of Tee et al. (*8*) (based on gas viscosities) may need adjustment to give better results for diffusion. This idea is tested in Models 11 and 12. In Model 11, Tee's constants b_1 and b_2 are retained, but a_1 and a_2 are fitted to the diffusion data; this gives very little improvement (s decreases from 0.039 to 0.038). In Model 12, all four constants (a_1, a_2, b_1, b_2) are fitted to the diffusion data, and a substantial improvement is found ($s = 0.029$, nearly comparable to Model 6). This comparison, like that of Models 1 and 6, indicates a discrepancy between Lennard-Jones parameters for viscosity and self-diffusion.

Discussion of Results (Other Systems)

The remaining four systems give the following standard deviations:

	Model 1	Model 3	Model 4	Model 5
CH_4-SF_6	0.0030	0.0028	0.0029	0.0029
CH_4-CH_3Cl	0.0257	0.0038	0.0045	0.0041
CH_3Cl-C_2H_5Cl	0.0248	0.0253	0.0256	...
N_2-n-C_4H_{10}	0.0308	0.0038	0.0072	0.0016

The prediction from viscosity (Model 1) is excellent for the nearly spherical pair CH_4–SF_6 and is systematically low for CH_4–CH_3Cl and N_2–n-C_4H_{10}. For the polar-polar pair, CH_3Cl–C_2H_5Cl, Model 1 with a Stockmayer potential describes the data within their uncertainty. Use of fitted parameters is a substantial improvement except for CH_3Cl–C_2H_5Cl. Model 3 is as good as Model 5 except for N_2-n-C_4H_{10}.

Conclusions

The Lennard-Jones potential allows prediction of D_{AB} from pure gas viscosities with a standard error of about 4%, provided that the combining rules are taken as in Model 1. Use of the geometric mean rule for σ_{AB} gives worse results.

The data can be reproduced within their uncertainty by using fitted values of σ_{AB} and ϵ_{AB}. These values are given in Table II.

The improvement of Model 6 over Model 1 and of Model 12 over Model 7 indicates that the Lennard-Jones potential needs different parameter values for self-diffusion than for viscosity. This is not surprising in view of the approximate nature of the Lennard-Jones model.

Nomenclature

a_1, a_2, b_1, b_2 = coefficients in Equations 2 and 3
c = molar density, mol/cm^3
D_{AB} = binary diffusion coefficient, cm^2/sec
$f_D{}^{(2)}$ = correction factor for second approximation of kinetic theory
M = mass number, g/mol
p = pressure, atm
s = relative standard error
T = absolute temperature, K
ϵ/k = potential energy parameter, K
σ = collision diameter, Å
ω = Pitzer acentric factor

Subscripts

A, B, i = chemical species
c = critical properties

Literature Cited

(1) Good, R. J., Hope, C. J., *J. Chem. Phys.*, **55**, 111 (1971).
(2) Gotoh, S., Manner, M., Sørensen, J. P., Stewart, W. E., *J. Chem. Eng. Data*, **19** (2), 169 (1974).
(3) Hirschfelder, J. O., Curtiss, C. F., Bird, R. B., "Mølecular Theory of Gases and Liquids," corrected printing with notes added, Wiley, New York, N.Y., 1964.
(4) Marrero, T. R., Mason, E. A., *J. Phys. Chem. Ref. Data*, **1**, 3 (1972).
(5) Mason, E. A., *J. Chem. Phys.*, **27**, 75 (1957).
(6) Monchick, L., Mason, E. A., *ibid.*, **35**, 1676 (1961).
(7) Reid, R. C., Sherwood, T. K., "The Properties of Gases and Liquids," 2nd ed., p 533, McGraw-Hill, New York, N.Y., 1966.
(8) Tee, L. S., Gotoh, S., Stewart, W. E., *Ind. Eng. Chem. Fundam.*, **5**, 356 (1966).
(9) Tee, L. S., Kuether, G. F., Robinson, R. C., Stewart, W. E., API Proceedings, Division of Refining, p 235, 1966.
(10) Trappeniers, N. J., Oosting, P. H., *Phys. Lett.*, **23**, 445 (1966).

Table II. Molecular Parameters Derived from Diffusion Measurements[a]

		Model 3			Model 4			Model 5		
System	N^b	σ	ϵ/k	s^c	σ	ϵ/k	s^c	σ	ϵ/k	s^c
CH_4–SF_6	6	4.454 ±0.009[d]	178.3	0.0028	4.451	179.1 ±2.1	0.0029	4.479 ±0.089	172.4 ±21.7	0.0029
CH_4–CH_3Cl	7	3.795 ±0.007	254.1	0.0038	3.844	238.8 ±2.1	0.0045	3.796 ±0.077	253.7 ±24.7	0.0041
CH_3Cl–C_2H_5Cl	5	4.174 ±0.009	418.5	0.0253	4.195	410.7 ±3.5	0.0256	[e]		
N_2-*n*-C_4H_{10}	4	4.461 ±0.011	162.5	0.0038	4.530	148.1 ±2.2	0.0072	4.393 ±0.108	177.9 ±24.8	0.0016
H_2–CH_4	3	3.317 ±0.009	73.9	0.0072	3.344	68.1 ±1.8	0.0068	3.371 ±0.151	62.9 ±29.4	0.0095
H_2–C_2H_6	3	3.712 ±0.010	89.0	0.0015	3.697	92.0 ±2.1	0.0016	3.708 ±0.122	89.8 ±25.7	0.0021
H_2–C_3H_8	3	4.057 ±0.011	93.5	0.0031	4.025	99.7 ±2.2	0.0042	4.088 ±0.136	87.5 ±25.8	0.0038
H_2-*n*-C_4H_{10}	3	4.270 ±0.012	108.5	0.0027	4.127	139.2 ±2.6	0.0059	4.228 ±0.123	117.1 ±25.8	0.0022
H_2-*i*-C_4H_{10}	3	4.259 ±0.012	112.0	0.0112	4.096	147.9 ±2.7	0.0030	4.068 ±0.112	154.6 ±27.5	0.0035
H_2–neo-C_5H_{12}	3	4.683 ±0.013	83.4	0.0212	4.717	78.4 ±2.1	0.0225	4.271 ±0.121	166.0 ±28.9	0.0016
CH_4–C_2H_6	3	4.069 ±0.011	173.1	0.0045	4.127	159.2 ±2.7	0.0077	3.999 ±0.112	191.5 ±30.0	0.0023
CH_4–C_3H_8	4	4.392 ±0.011	181.8	0.0113	4.455	167.1 ±2.5	0.0145	4.176 ±0.113	239.6 ±32.7	0.0033
CH_4-*n*-C_4H_{10}	3	4.565 ±0.012	211.0	0.0044	4.556	213.3 ±3.0	0.0040	4.479 ±0.141	232.7 ±37.1	0.0021
CH_4-*i*-C_4H_{10}	3	4.544 ±0.012	217.9	0.0048	4.526	222.6 ±3.1	0.0040	4.460 ±0.144	239.5 ±38.2	0.0036
CH_4–neo-C_5H_{12}	3	5.110 ±0.014	162.2	0.0121	5.147	155.5 ±2.7	0.0138	4.852 ±0.146	217.7 ±33.8	0.0005
C_2H_6–C_3H_8	3	4.718 ±0.013	218.9	0.0228	4.808	198.8 ±3.1	0.0269	4.134 ±0.265	396.3 ±101.1	0.0055
C_2H_6-*n*-C_4H_{10}	3	4.919 ±0.013	254.1	0.0253	4.909	257.6 ±3.3	0.0248	[e]		
C_2H_6-*i*-C_4H_{10}	3	4.842 ±0.013	262.3	0.0142	4.879	253.7 ±3.4	0.0156	4.411 ±0.283	392.3 ±102.0	0.0006
C_2H_6–neo-C_5H_{12}	3	5.461 ±0.015	195.3	0.0169	5.500	188.4 ±2.9	0.0185	5.030 ±0.210	293.4 ±55.0	0.0006
C_3H_8-*n*-C_4H_{10}	2	5.294 ±0.017	266.9	0.0312	5.237	281.7 ±4.4	0.0299	[e]		
C_3H_8-*i*-C_4H_{10}	3	5.154 ±0.014	275.5	0.0281	5.207	263.6 ±3.4	0.0300	[e]		
C_3H_8–neo-C_5H_{12}	3	5.770 ±0.016	205.1	0.0228	5.828	195.2 ±3.0	0.0250	5.089 ±0.289	367.1 ±86.8	0.0017
n-C_4H_{10}–neo-C_5H_{12}	3	5.598 ±0.015	238.1	0.0244	5.929	173.8 ±2.8	0.0112	6.209 ±0.174	129.1 ±25.9	0.0007
i-C_4H_{10}–neo-C_5H_{12}	3	5.852 ±0.016	245.8	0.0122	5.899	236.7 ±3.3	0.0134	5.591 ±0.210	303.1 ±47.6	0.0123

[a] To be used with the Lennard-Jones (12-6) potential, except that the Stockmayer (12-6-3) potential is used for the systems CH_4–CH_3Cl and CH_3Cl–C_2H_5Cl. The models are defined as in Table I, with the combining rules extended as in (*3*, pp 222–3) for the systems CH_4–CH_3Cl and CH_3Cl–C_2H_5Cl. [b] N is the number of diffusivity data for the given system. [c] s is the standard deviation based on logarithmic residuals, $\ln(D_{AB,\text{pred}}/D_{AB,\text{obsd}})$. [d] Values preceded by ± are one-parameter 95% confidence limits calculated by linearization with an error variance $s^2 = (0.0045)^2$ (Table I, Model 5). [e] Results for these cases are omitted because of large uncertainties in the fitted constants.

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Supplementary Material Available. Tables 3–5 will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JCED-74-172.