Binary Diffusion Coefficients of Low-Density Gases
I. Measurements by Modified Loschmidt Method

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Binary diffusion coefficients of 24 equimolar gas mixtures were determined at atmospheric pressure and 298–438K, with a probable accuracy of 1%. The data were obtained in a modified Loschmidt cell equipped with a recording optical interferometer. The components studied were H_2, N_2, SF_6, CH_3Cl, C_2H_5Cl, and paraffins from methane to neo-pentane. The molecular interpretation of the data is considered in Part II.

Binary diffusion coefficients are useful in engineering studies of reaction, separation, and mixing processes. They also are useful for testing molecular theories and prediction methods. New measurements, based on an improved form of the Loschmidt method, are given here for 24 different pairs of gases.

Twenty of the gas pairs studied here are paraffin or hydrogen–paraffin systems. The homologous relationships among these pairs will be exploited in Part II. The other four pairs, originally studied by Manner (*5*), provide comparison with previous measurements (for N_2-n-C_4H_{10}) and a test of prediction methods for nearly spherical molecules (CH_4 and SF_6), as well as polar ones (CH_3Cl and C_2H_5Cl). The recent survey by Marrero and Mason (*6*) indicates a lack of data, or narrow temperature range of data, for all of these systems except H_2–CH_4.

Experimental

The measurements were done in a modified Loschmidt cell of rectangular cross section (*3*), adapted from the design of Boyd et al. (*1*). The present design differs from that of Boyd et al., mainly in the use of a more compact and sensitive interferometer (*5*), equipped for continuous recording and operable over a wide temperature range. Small thermocouples mounted inside the cell facilitate prerun equilibration, as well as detection of small temperature changes caused by the diffusion-thermo effect (*2, 3*). The latter disturbances were appreciable only for the hydrogen–paraffin systems, which gave changes up to 1.0°C, decaying to less than 0.01°C after the first 2 or 3 min of diffusion. The apparatus and its operation have already been fully described (*2, 3, 5*).

Diffusing Gases

The gases used are listed in Table I, along with the manufacturers' purity specifications. The effect of the impurities has been examined with the theory of Stewart and Prober (*10*); the effect is of the order 0.2% of D_{AB} or less for the present systems and is accordingly neglected.

Table I also gives molecular parameters for calculation of predicted diffusivities. Two sets are given for each substance: one for finding the transport integrals and the other for finding the mixture density.

Data Analysis

The optical fringe data from each diffusion test were digitized as previously described (*3*), along with the temperature and pressure values. Fringe readings throughout the tests were used, except that in hydrogen systems the first 10% of the fringes were omitted because of the difusion-thermo effect mentioned above.

The theory of Stewart et al. (*9*) was fitted to the data of each experiment by a weighted least-squares calculation (*3*). The corrections for composition dependence of D_{AB} and molar density c were calculated from the parameters of Table I, with the combining rules of Hirschfelder et al. (*4*). This calculation yielded the following six fitted parameters for each experiment: $(D_{AB})_0$ = binary diffusivity at run temperature T, initial cell pressure p_0, and reference composition $x_{A0} = 0.5$; Y_I = fringe number at start of test; $(R_B - R_A)$ = molar refraction difference; K_1, K_2, $k_B\Lambda_B$ = dimensionless absorption constants. The theory of Stewart et al. (*9*) requires $k_B\Lambda_B \geq 0$; this inequality was included in the computer program. Inclusion of the measured pressure change, Δp, in the least-squares analysis proved essential to obtain well-conditioned equations for the six parameters (five if the best fit lay on the boundary $k_B\Lambda_B = 0$).

The calculated results are summarized in Table II for 84 diffusion experiments. The first 10 experiments are by Manner (*5*), and the remaining 74 by Gotoh (*2*). The present results supersede the calculations of Manner (*5*)

Table I. Information on Gaseous Components

	Molecular parameters[a]				Purity, min mol %
Substance	σ, Å	ϵ/k, K	δ_{max}	Ref.	
H_2	2.915	38.0	0.	μ, *4*	99.94[b]
	2.959	36.7	0.	*B*, *4*	
CH_4[c]	3.774	143.81	0.	μ, *12*	99.67[d]
	4.010	142.87	0.	*B*, *12*	
C_2H_6	4.480	208.46	0.	μ, *12*	99.99[d]
	5.220	194.14	0.	*B*, *12*	
C_3H_8	5.136	229.93	0.	μ, *12*	99.5[b]
	5.711	233.28	0.	*B*, *12*	
n-C_4H_{10}	5.339	309.74	0.	μ, *12*	99.5[b]
	7.152	233.74	0.	*B*, *12*	
i-C_4H_{10}	5.278	330.1	0.	μ, *11*	99.5[b]
	6.65	237.	0.	*B*, *12* (correl. viii)	
neo-C_5H_{12}	6.520	183.02	0.	μ, *12*	99.88[d]
	7.420	233.66	0.	*B*, *12*	
N_2	3.722	85.23	0.	μ, *12*	99.998[e]
	3.694	96.26	0.	*B*, *12*	
CH_3Cl	3.94	414.	0.5	μ, *8*	99.5[b]
	3.43	380.	0.85	*B*, *8*	
C_2H_5Cl	4.45	423.	0.4	μ, *8*	99.7[b]
	5.41	320.	0.28	*B*, *8*	
SF_6	5.128	222.1	0.	μ, *11*	98.7[b]
	5.910	188.7	0.	*B*, *4*	

[a] To be used in the Stockmayer (12-6-3) potential, or the Lennard-Jones (12-6) potential if $\delta_{max} = 0$. [b] Matheson Co., Inc. [c] The polarizability of CH_4 was taken as 26.0×10^{-25} cm^3 (*4*) for calculation of the system CH_4-CH_3Cl. [d] Phillips Petroleum Co. [e] Air Products and Chemicals, Inc.

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Table II. Summary of Measured and Predicted Values

Components	T, K	p_0, mm Hg	Δp, mm Hg	N_p[a]	s, fringes	$D_{AB,\text{obsd}}$, cm^2/sec	Dev, %[b]
CH_4–SF_6	297.6	747.6	0.0	6	0.033	0.1145	−2.4
	357.9	733.5	0.5	5	0.021	0.1617	−0.1
	418.2	742.8	0.8	5	0.041	0.2121	0.4
	477.9	729.4	1.2	5	0.043	0.2768	−0.1
CH_4–CH_3Cl	297.6	740.0	−2.7	6	0.029	0.1458	−3.0
	358.0	738.5	−1.9	6	0.025	0.2090	−2.6
	418.2	744.7	−1.4	6	0.037	0.2795	−2.6
	477.8	735.2	−0.4	5	0.050	0.3632	−2.4
CH_3Cl–C_2H_5Cl	357.9	741.9	−4.9	6	0.036	0.08656	−1.8
	418.5	741.0	−3.0	6	0.027	0.1216	−3.8
CH_4–SF_6	298.2	739.0	0.5	5	0.028	0.1136	−0.1
	378.1	745.3	0.5	5	0.029	0.1757	0.2
	438.3	737.8	0.4	5	0.043	0.2323	0.6
CH_4–CH_3Cl	298.2	738.5	−5.9	6	0.019	0.1453	−2.1
	378.2	743.1	−1.5	5	0.034	0.2297	−2.0
	438.4	733.3	−1.0	5	0.059	0.3112	−2.8
CH_3Cl–C_2H_5Cl	298.3	735.8	−25.6	6	0.061	0.05767	2.0
	298.2	730.5	−23.1	6	0.064	0.05851	1.3
	378.2	740.9	−4.3	6	0.030	0.1003	−5.0
	438.4	731.1	−1.7	5	0.037	0.1336	−2.5
N_2–n-C_4H_{10}	298.1	740.7	−3.1	6	0.032	0.1012	−2.7
	298.2	734.3	4.3	6	0.035	0.1021	−2.7
	378.2	737.6	−0.2	5	0.040	0.1596	−3.4
	438.3	730.9	0.3	5	0.106	0.2106	−3.3
H_2–CH_4	298.0	730.8	−0.5	5	0.080	0.7811	−2.2
	378.3	737.8	−0.3	5	0.073	1.153	−0.8
	438.4	742.7	−0.9	5	0.073	1.490	−1.9
H_2–C_2H_6	298.0	738.7	0.1	5	0.137	0.5708	0.7
	378.3	740.6	0.0	5	0.082	0.8646	0.9
	438.4	734.3	−0.4	5	0.092	1.129	0.6
H_2–C_3H_8	298.0	732.7	2.2	5	0.182	0.4712	1.3
	378.1	736.6	0.2	5	0.132	0.7103	1.9
	438.5	739.9	−0.3	5	0.128	0.9190	1.5
H_2–n-C_4H_{10}	298.0	736.5	1.1	5	0.231	0.3997	7.4
	378.2	738.8	0.1	5	0.248	0.6155	6.8
	438.4	735.9	0.3	5	0.124	0.8010	7.0
H_2–i-C_4H_{10}	298.0	741.5	1.0	5	0.189	0.3924	9.3
	378.2	729.0	0.4	5	0.195	0.6202	8.1
	438.4	738.2	−0.1	5	0.135	0.8051	6.8
H_2–neo-C_5H_{12}	298.0	733.1	2.8	5	0.220	0.3515	0.8
	378.3	740.6	1.7	5	0.272	0.5443	−1.8
	438.4	741.7	0.3	5	0.101	0.7136	−3.4
CH_4–C_2H_6	298.0	733.6	0.8	5	0.028	0.1615	−2.3
	378.2	739.8	−0.2	5	0.028	0.2520	−3.0
	437.8	743.9	−1.8	5	0.045	0.3274	−3.0
CH_4–C_3H_8	298.0	735.6	0.7	5	0.093	0.1262	−1.2
	378.2	737.8	−0.3	5	0.043	0.2013	−3.1
	437.6	738.5	−1.1	5	0.072	0.2639	−3.4
	438.4	733.2	−0.9	5	0.095	0.2669	−3.5
CH_4–n-C_4H_{10}	298.3	731.4	−1.1	6	0.047	0.1079	0.9
	378.2	737.6	−0.4	5	0.079	0.1704	0.1
	436.3	733.3	−1.4	5	0.098	0.2243	0.1
CH_4–i-C_4H_{10}	298.0	735.2	0.6	5	0.040	0.1067	1.4
	378.3	729.2	−0.1	5	0.071	0.1722	0.4
	436.3	733.5	−1.4	5	0.089	0.2236	0.6
CH_4–neo-C_5H_{12}	298.0	734.5	−0.1	6	0.023	0.09219	−0.1
	378.2	741.9	0.4	5	0.079	0.1452	−1.7
	436.2	733.5	−0.2	5	0.093	0.1923	−2.5
C_2H_6–C_3H_8	298.0	740.8	−1.8	5	0.015	0.08041	−1.2
	378.2	741.3	−0.8	5	0.027	0.1316	−4.3
	437.6	737.7	−2.8	5	0.032	0.1760	−5.4
C_2H_6–n-C_4H_{10}	298.0	733.4	−3.3	5	0.059	0.06597	3.1
	378.2	736.3	−0.6	5	0.072	0.1085	0.1
	437.2	737.4	−3.2	5	0.053	0.1460	−1.9
C_2H_6–i-C_4H_{10}	298.0	731.8	0.3	6	0.035	0.06814	0.0
	378.2	734.1	−0.5	5	0.056	0.1106	−1.6
	436.9	735.6	−2.7	5	0.031	0.1476	−2.8

Table II. Continued

Components	T, K	p_0, mm Hg	Δp, mm Hg	N_p[a]	s, fringes	$D_{AB,\mathrm{obsd}}$, cm^2/sec	Dev, %[b]
C_2H_6–neo-C_5H_{12}	298.0	735.3	−3.5	6	0.028	0.05827	0.4
	378.1	744.5	−0.3	5	0.041	0.09290	−1.6
	436.1	734.4	−2.1	5	0.056	0.1247	−2.9
C_3H_8–n-C_4H_{10}	378.2	737.3	−1.6	5	0.047	0.07921	4.5
	437.7	745.7	−4.1	6	0.039	0.1086	0.0
C_3H_8–i-C_4H_{10}	298.0	739.7	−2.1	6	0.024	0.05066	1.0
	378.2	738.8	−1.1	6	0.020	0.08463	−2.6
	437.8	745.7	−3.1	6	0.028	0.1136	−4.5
C_3H_8–neo-C_5H_{12}	298.1	736.7	−6.4	6	0.019	0.04450	0.4
	378.2	741.9	−1.6	6	0.028	0.07199	−2.1
	437.7	737.4	−3.6	6	0.037	0.09736	−4.1
n-C_4H_{10}–neo-C_5H_{12}	298.0	733.5	−12.7	6	0.096	0.04283	−13.2
	378.3	741.9	−2.1	6	0.054	0.06598	−10.4
	437.8	741.0	−5.1	6	0.028	0.08607	−8.9
i-C_4H_{10}–neo-C_5H_{12}	298.1	746.6	−8.7	6	0.038	0.03682	−1.1
	378.2	741.6	−1.7	6	0.020	0.05940	−0.7
	437.7	746.7	−4.0	6	0.027	0.07999	−2.9

[a] N_p is the number of parameters fitted by least squares, using the model of Gotoh et al. (3). When $N_p = 5$, the absorption term $k_B\Lambda_B$ is zero. [b] Deviation, % = $100 \times [D_{AB,\mathrm{pred}} - D_{AB,\mathrm{obsd}}]/D_{AB,\mathrm{obsd}}$.

and Gotoh (*2*), which were done before the detailed model of the Loschmidt experiment [Gotoh et al. (*3*); Stewart et al. (*9*)] was completed.

Discussion of Results

Along with the measured diffusivity $(D_{AB})_0$ for each test, Table II gives the measured pressure change, Δp, and the standard deviation, s, obtained in fitting the fringe readings. Data with small Δp and small s are considered to be the best.

Replicate tests included in Table II give the following comparisons when corrected for differences in temperature and initial pressure:

	T, K	Diff of corrected D_{AB} values, %
CH_4–SF_6	298	2.3
CH_4–CH_3Cl	298	1.0
N_2–n-C_4H_{10}	298	0.0
CH_3Cl–C_2H_5Cl	298	0.8
CH_4–C_3H_8	438	0.1

The first two comparisons are between the data of Gotoh (*2*) and Manner (*5*) and include differences in experimental techniques. The last three comparisons are from Gotoh (*2*).

Our data for H_2–CH_4 may be compared with the reference correlation of Marrero and Mason (*6*). The differences (calculated as in Table II) are as follows:

T, K	Dev, %
298.0	−2.98
378.3	−0.75
438.4	−0.90

Our results are in better accord with the data plotted by Marrero and Mason (*6*) than with the reference line given there.

Our results for N_2–n-C_4H_{10} have been compared (*3*) with measurements of other workers. Two recent measurements lie within 1.1% of ours.

From these comparisons, it appears that the data of Table II are accurate within 1% for $s < 0.1$ and 2% for $s < 0.2$. The first ten data were obtained during the development of the technique and are accordingly somewhat less accurate.

Predicted values of D_{AB} were calculated to the second Kihara approximation (*7*), with the collision integrals of Monchick and Mason (*8*) and the combining rules recommended by Hirschfelder et al. (*4*, p 223). The deviations of these predictions from our measurements are shown in Table II. The deviations show trends which suggest that the potential model could be improved.

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