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Prediction of the Temperature Dependence of Binary Diffusion Coefficients of Gaseous Systems from Thermal Diffusion Factors and Diffusion Coefficients at 300 K[1]

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Data are presented which enable binary diffusion coefficients and their concentration dependences to be predicted from diffusion coefficients and thermal diffusion factors at 300 K. The results up to 2000 K are compared with corresponding values derived from the compilation of Mason and Marrero.

KEY WORDS: Chapman Enskog theory; diffusion coefficient; dilute gases; Kihara first approximation; thermal diffusion factors.

1. INTRODUCTION

Using the basic theory reported by Humphreys and Mason [1], we recently derived [2, 3] equations relating the temperature dependence of limiting binary diffusion coefficients to corresponding limiting thermal diffusion factors and viscosities. Even though these relations should be valid only over the same temperature range used to measure the thermal diffusion factors, the predicted diffusion coefficients appear to be quite accurate from room temperature to 2000 K or higher. The purpose of this paper is to report information for predicting diffusion coefficients for many systems studied in this laboratory and, where possible, to compare the results with the compilation of Mason and Marrero [4], which represents the results of those systems which were reported in the literature up to 1971.

This paper should be read in close conjunction with Refs. 2 and 3.

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2. THEORY

In previous papers [2, 3] the first Kihara approximation [5] for the thermal diffusion factor, α_T, together with several relationships from the Chapman-Enskog theory [5], were used to deduce the relationship

$$\ln[\mathscr{D}^0_{12}(T_2)/\mathscr{D}^0_{12}(T_1)] = [1-(4\bar{K}_2C_0)^{-1}]\ln(T_2/T_1) \tag{1a}$$

or

$$\mathscr{D}^0_{12}(T_2) = \mathscr{D}^0_{12}(T_1)[T_2/T_1]^a \tag{1b}$$

where the $\mathscr{D}^0_{12}$ are limiting coefficients when the mole fraction of heavy component, x_1, is zero and

$$a = 2[1-(4\bar{K}_2C_0)^{-1}] \tag{1c}$$

In Eq. (1c) C_0, the reciprocal of $(\alpha^0_T)_0$, the zero-pressure thermal diffusion factor when $x_1 = 0$, is assumed to be constant. The quantity $\bar{K}_2$ is the mean value of

$$K_2 = -(S_2/Q_2) \tag{2a}$$

over the temperature range used to measure C_0, and

$$-S_2 = \frac{15}{2}M_2\frac{(M_1-M_2)}{(M_1+M_2)^2} + \frac{4M_1M_2}{(M_1+M_2)}A^*_{12} - \frac{5}{3}\frac{M_2^2}{(M_1+M_2)}\frac{P\mathscr{D}^0_{12}}{RT\eta_2} \tag{2b}$$

and

$$Q_2 = \frac{10}{3}\frac{M_2}{(M_1+M_2)^2}\frac{P\mathscr{D}^0_{12}}{RT\eta_2}\left(3M_1^2 + \beta M_2^2 + \frac{8}{5}M_1M_2A^*_{12}\right) \tag{2c}$$

In Eqs. (2b) and (2c) $\mathscr{D}^0_{12}$ and η_2, the viscosity of light component 2, are used to replace two reduced collision integrals with experimental quantities, and A^*_{12}, a ratio of other collision integrals, is approximately 1.1 and essentially independent of temperature and the form of the interaction potential: β is unity for the Kihara first approximation and close to 1.2 for the first Chapman-Cowling approximation [5], M_1 and M_2 are the molar masses, and R is the gas constant. Both the Kihara and the Chapman-Cowling first approximations yield identical results when $x_1 = 0$. Thus if $(\alpha^0_T)_0$ is constant, Eq. (1b) may be used to calculate the temperature dependence of $\mathscr{D}^0_{12}$ from the value at T_1 (taken here to be 300 K) and the constant "a," which is calculated from experimental quantities.

Table I. Values of the Experimental Quantities C_0 and C_1 and the Derived Constants a and b at 300 K^{a,b}

System	$\mathscr{D}^0_{12}$(300 K)	C_0	C_1	a	b	Ref. No.(s.)
He-Ne	1.094_0	2.43_0	1.47_5	1.68_3	1.70_2	13, 14
He-Ar	0.734_4	1.45_6	2.13_5	1.69_1	1.70_1	13, 14
He-Kr	0.635_6	1.18_2	2.15_6	1.69_1	1.69_0	13, 14
He-Xe	0.542_9	0.97_0	2.30_8	1.68_5	1.68_8	13, 14
Ne-Ar	0.323_4	4.27_6	2.65_9	1.72_5	1.72_8	13, 14
Ne-Kr	0.262_9	2.27_6	2.41_5	1.73_1	1.73_6	13, 14
Ne-Xe	0.221_2	1.72_7	2.66_5	1.73_6	1.74_2	13, 14
H_2-Ne	1.17_6	2.75_4	0.87_9	1.70_3	1.71_0	15
D_2-Ne	0.871_3	3.32_6	0.81_4	1.70_4	1.72_2	16
H_2-Ar	0.824_0	2.11_0	2.28_4	1.74_7	1.76_5	15
D_2-Ar	0.594_2	2.32_0	2.34_1	1.75_1	1.77_1	16
H_2-Kr	0.724_0	1.91_7	2.79_0	1.76_3	1.78_4	15
D_2-Kr	0.518_2	2.03_7	2.75_5	1.76_9	1.78_5	16
H_2-Xe	0.622_3	1.74_9	3.13_3	1.77_9	1.79_3	15
D_2-Xe	0.446_5	1.80_5	3.16_1	1.78_0	1.79_4	16
He-N_2	0.706_7	1.51_4	2.37_9	1.69_9	1.71_4	17
H_2-N_2	0.784_4	1.96_2	2.28_0	1.73_4	1.75_4	18
D_2-N_2	0.579_6	2.35_5	2.38_0	1.74_8	1.76_6	18
He-O_2	0.744_0	1.60_1	2.16_5	1.70_7	1.70_9	19
H_2-O_2	0.826_6	2.15_3	2.28_6	1.74_8	1.76_6	18
D_2-O_2	0.606_9	2.52_1	2.26_0	1.75_9	1.77_2	18
He-CO	0.702_3	1.99_4	2.27_2	1.71_0	1.71_5	19
H_2-CO	0.775_0	1.55_8	2.35_8	1.74_2	1.75_5	20
H_2-He	1.597_0	7.70_0	0.00_0	1.68_1	1.74_2	21, 22
He-CO_2 *	0.603_0	1.20_0	2.46_0	1.70_0	1.70_8	23, 24
He-N_2O	0.593_5	1.19_6	2.55_0	1.70_1	1.71_4	23
Ne-COS	0.540_1	0.95_1	2.45_4	1.66_7	1.69_1	23
He-SF_6 *	0.389_4	0.68_2	2.50_0	1.68_0	1.68_0	24, 25
He-C_4F_8 *	0.287_7	0.50_0	2.83_0	1.68_0	1.69_5	26, 27
N_2-Ne	0.339_8	11.06_4	7.51_2	1.81_9	1.83_5	17
N_2-Ar	0.203_4	13.47_2	-0.75_0	1.72_7	1.72_6	17
N_2-Kr	0.159_5	6.55_3	1.36_6	1.83_3	1.82_4	17
N_2-Xe	0.131_7	5.24_3	2.59_4	1.85_9	1.84_8	17
CH_4-Ar	0.219_5	9.47_3	-0.05_1	1.82_8	1.83_4	28
CH_4-Kr	0.178_7	7.38_3	2.27_3	1.87_8	1.88_2	28
CH_4-Xe	0.148_2	7.49_0	4.22_0	1.91_0	1.90_8	28
CO-Ne	0.344_6	9.97_0	6.93_7	1.79_4	1.82_0	19
CO-Ar	0.206_7	15.41_7	-0.10_8	1.75_4	1.77_4	19

Table I. *(Continued)*

System	$\mathscr{D}^0_{12}$ (300 K)	C_0	C_1	a	b	Ref. No.(s.)
He–CH_4 *	0.680_8	1.78_8	2.91_8	1.71_9	1.73_2	29, 30
He–CH_3F *	0.611_3	1.28_4	2.60_4	1.71_9	1.73_2	29, 30
He–CH_2F_2 *	0.552_0	1.09_1	2.49_4	1.70_3	1.71_8	29, 30
He–CHF_3 *	0.510_3	0.94_0	2.51_5	1.70_0	1.70_4	29, 30
He–CF_4 *	0.480_9	0.85_3	2.51_5	1.67_8	1.69_3	29, 30
He–C_2H_6 *	0.499_8	1.03_4	2.79_5	1.69_4	1.70_9	3, 31
He–C_2H_5F *	0.465_0	0.90_8	2.69_9	1.69_5	1.70_4	3, 31
He–1,1-$C_2H_4F_2$ *	0.436_3	0.82_4	2.71_3	1.69_2	1.70_4	3, 31
He–1,1,1-$C_2H_3F_3$ *	0.416_0	0.77_6	2.65_4	1.69_3	1.69_8	3, 31
He–1,1,2-$C_2H_3F_3$ *	0.414_8	0.76_4	2.70_3	1.68_9	1.70_1	3, 31
He–1,1,1,2-$C_2H_2F_4$ *	0.396_0	0.70_9	2.70_4	1.68_3	1.69_8	3, 31
He–1,1,2,2-$C_2H_2F_4$ *	0.397_0	0.71_1	2.66_0	1.68_8	1.69_6	3, 31
He–C_2HF_5 *	0.379_0	0.68_4	2.65_4	1.68_8	1.69_3	3, 31
He–C_2F_6 *	0.365_8	0.66_2	2.62_9	1.69_0	1.69_0	3, 31

[a] The values of C_0 and C_1 designated with an asterisk correspond to zero pressure; the remainder, to a pressure of 0.32 atmosphere. Refer to Refs. 29 and 31 for the pressure dependencies of C_0 and C_1 for the helium–fluoromethane and helium–fluoroethane systems.

[b] Units of $\mathscr{D}^0_{12}$: $cm^2 \cdot s^{-1}$.

The analogous relation to Eq. (1b), for the case when $x_1 = 1$, is

$$\mathscr{D}^1_{12}(T_2) = \mathscr{D}^1_{12}(T_1)[T_2/T_1]^b \tag{3a}$$

$$b = 2[1 - [4\bar{K}_1(C_0 + C_1)]^{-1}] \tag{3b}$$

where $(C_0 + C_1)$ is the reciprocal of $(\alpha^1_T)_0$, the zero-pressure thermal diffusion factor for $x_1 = 1$. The constants C_0 and C_1 are obtained experimentally by means of the linear relationship first proposed by Laranjeira [6]

$$(\alpha_T)^{-1} = C_0 + C_1 x_1$$

Both C_0 and C_1 [and hence $(\alpha^0_T)_0$ and $(\alpha^1_T)_0$] are pressure dependent; an estimate of their variation with pressure can be obtained from the approximate theory of Oost et al. [7]. The values of C_0 and C_1, designated with asterisks in Table I were obtained by extrapolating the experimental results to zero pressure; the remaining values correspond to a pressure of 0.32 atm.

When $x_1 = 1$, only the first Kihara approximation for α_T gives values of $\mathscr{D}^1_{12}$ which, when combined with corresponding values of $\mathscr{D}^0_{12}$, yield sensible results for the concentration dependence $(\mathscr{D}^1_{12}/\mathscr{D}^0_{12})$; use of the Chapman–Cowling first approximation predicts, in disagreement with experiment, that $\mathscr{D}_{12}$ decreases with *increasing* concentration of the heavy component. Thus Eq. (1b) enables the temperature dependence of $\mathscr{D}^0_{12}$ to be calculated from the data in Table I: the values of *a* were calculated from Eqs. (1c), (2b), and (2c) with the aid of the viscosity data [8–11] for pure components at 300 K. Equation (3a) may be used to calculate the temperature dependence of $\mathscr{D}^1_{12}$: the values of $\mathscr{D}^1_{12}(300\ \mathrm{K})$ may be found in the references listed in the last column in Table I.

Table II lists the percentage differences between the values of $\mathscr{D}^0_{12}$ calculated from Eq. (1b) and the corresponding values given by the compilation of Mason and Marrero [4], which does not contain all the systems in Table I. In general these differences are within the error limits suggested by Mason and Marrero.

Table II. Percentage Differences Between the Values of $\mathscr{D}^0_{12}$ Predicted by Eq. (1b) and the Corresponding Values from the Compilation of Mason and Marrero [4]

System	300 K	1000 K	2000 K
He-Ne	0.7 (−0.1)	−1.6 (2.3)	−4.2 (4.2)
He-Ar	−0.5 (0.0)	−5.7 (0.5)	−9.9 (0.0)
He-Kr	−0.5 (−0.2)	−4.5 (0.6)	−9.6 (0.0)
He-Xe	−0.7 (−0.2)	−3.1 (0.5)	−8.5 (0.0)
Ne-Ar	0.0	1.2	1.5
Ne-Kr	0.2	−0.5	0.0
Ne-Xe	0.5	0.6	0.7
H_2-He	3.2	−2.7	−7.9
H_2-Ne	4.4	1.0	−0.9
H_2-Ar	−0.2	−3.2	−2.7
H_2-Kr	3.4	2.1	2.7
H_2-Xe	4.9	9.2	13.5
H_2-N_2	1.5	1.5	0.6
H_2-O_2	3.2	5.2	6.2
H_2-CO	−0.5	1.5	1.6
He-N_2	−0.8	−2.0	−4.1
He-O_2	0.9	0.4	0.2
He-CO	−1.7	−1.6	−2.8
He-CO_2	2.9	−0.8	−2.4
He-H_2	3.0	0.0	−3.4
N_2-Ne	3.0	13.0	18.6
N_2-Ar	2.9	0	−1.8
N_2-Kr	3.1	11.5	17.0
N_2-Xe	3.7	12.9	18.5
He-SF_6	−2.9	3.6	7.5
CH_4-He	1.1	−1.8	−4.2
CH_4-Ar	7.3	12.5	16.0

The values in parentheses for the first four systems in Table II are the percentage differences between the results calculated from the data in Table I and the corresponding values calculated from the potential functions of Keil et al. [12] with recent differential scattering cross sections and diffusion data.

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