η, ρ, solution surface tension, viscosity, and density; Θ, limiting wetting angle; r, mean pore radius; g, acceleration of gravity; α, inclination of wick to horizontal.

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A COMPARISON OF METHODS OF COMBINING FORCE PARAMETERS

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A study is made of two models for the molecular-interaction potential in calculating diffusion coefficients for binary vapor—gas systems.

One needs information on diffusion coefficients (DC) for binary vapor—gas systems for calculations on chemical engineering processes [1], so one needs methods of forecasting DC. The kinetic theory of gases gives DC from the following equation [2-4]:

$$D_t = \frac{1{,}883(10)^{-24}\sqrt{T^3\left(\frac{1}{M_1}+\frac{1}{M_2}\right)}}{p\sigma_{12}^2\Omega_D}, \tag{1}$$

where the combination relations used are [2-9]:

$$\sigma_{12} = (\sigma_1+\sigma_2)/2,\ \varepsilon_{12} = (\varepsilon_1\varepsilon_2)^{1/2}; \tag{2}$$

$$\sigma_{12} = (\sigma_1+\sigma_2)/2,\ \varepsilon_{12} = (\varepsilon_1\sigma_1^6\varepsilon_2\sigma_2^6)^{1/2}/\sigma_{12}^6; \tag{3}$$

$$\sigma_{12} = (\sigma_1+\sigma_2)/2,\ \ \varepsilon_{12} = 2\varepsilon_1\varepsilon_2/(\varepsilon_1+\varepsilon_2); \tag{4}$$

$$\sigma_{12} = (\sigma_1+\sigma_2)/2,\ \varepsilon_{12}\sigma_{12}^{12} = \frac{\varepsilon_1\sigma_1^{12}}{2^{13}}\left[1+\left(\frac{\varepsilon_2\sigma_2^{12}}{\varepsilon_1\sigma_1^{12}}\right)^{1/13}\right]^{13}; \tag{5}$$

$$\sigma_{12}^6\varepsilon_{12} = (\varepsilon_1\sigma_1^6\varepsilon_2\sigma_2^6)^{1/2},\ \varepsilon_{12}\sigma_{12}^{12} = \frac{\varepsilon_1\sigma_1^{12}}{2^{13}}\left[1+\left(\frac{\varepsilon_2\sigma_2^{12}}{\varepsilon_1\sigma_1^{12}}\right)^{1/13}\right]^{13}. \tag{6}$$

We have calculated DC for two molecular interaction potentials: the 6-12 Lennard-Jones one and the Kessel'man effective potential [7]. The collision integral Ω_D is defined by [3]

$$\Omega_D = \frac{A}{(T^*)^B}+\frac{C}{\exp ET^*}+\frac{G}{\exp FT^*}+\frac{L}{\exp HT^*}, \tag{7}$$

where $T^* = kT/\varepsilon_i$; A = 1.06036; B = 0.15610; C = 0.19300; E = 0.47635; G = 1.03587; F = 1.52996; L = 1.76474; H = 3.89411. The values of σ_i and ε_i for pure substances were taken from the literature for the first model (Table 1), while for the second they were determined graphically from [7]. Figure 1 shows the results. The deviations are given by

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TABLE 1. Parameters in the 6-12 Lennard-Jones Potentials Calculated from Viscosities

Substance	Force constants			Substance	Force constants		
	$\sigma_i \cdot 10^{10}$, m	ε_i/k, K	source		$\sigma_i \cdot 10^{10}$, m	ε_i/k, K	source
Argon	3,418	124,0	[4]	Octane	7,451	320,0	[4]
Helium	2,556	10,22	[4]	Nonane	8,448	240,0	[4]
Carbon dioxide	3,897	213,0	[4]	Benzene	5,270	440,0	[4]
Pentane	5,769	345,0	[4]	Methanol	3,626	481,8	[3]
Hexane	5,909	413,0	[4]	1-Propanol	4,549	576,7	[3]
Heptane*	8,88	282,0	[4]	Acetone	4,600	560,2	[3]

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*Parameters calculated from the second virial coefficients.

TABLE 2. Comparison of Combination Methods

Diffusion gas	Mean and maximal deviations† on using combination rules (2)-(6)											
	6-12 Lennard-Jones potential						Kessel'man effective potential					
	No. of systems*	(2)	(3)	(4)	(5)	(6)	No. of systems*	(2)	(3)	(4)	(5)	(6)
Carbon dioxide	7	11 37	7 10	8 23	10 22	4 13	7	8 12	5 8	5 11	10 14	5 7
Argon	7	8 20	5 7	8 18	15 22	5 14	6	5 9	6 13	10 24	10 14	7 13
Helium	7	13 39	20 50	35 70	8 22	10 27	9	30 42	34 56	65 85	9 23	12 29

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*Corresponds to Fig. 1.

†The upper number is the mean deviation and the lower is the maximal one of the calculated values from the measurements given in the published sources quoted in the text.

$$\Delta_j = \frac{D_j - D_{\tau j}}{D_j} \cdot 100, \quad \bar{\Delta} = \frac{1}{n} \sum_{j=1}^{n} |\Delta_j|. \tag{8}$$

For comparison, we used data on the diffusion of the following in carbon dioxide: pentane [11, 15], hexane [11], heptane [11], octane [11], nonane [11], benzene [11, 12, 15-17], toluene [11]; we also used values for diffusion in argon of: pentane [11, 18-20], hexane [11, 19-22], heptane [11, 20, 23], octane [11, 20, 21, 23], nonane [11], benzene [11, 16], toluene [11, 14, 16], and acetone [11, 16]; for diffusion in helium of: pentane [13, 18, 19], hexane [13, 19, 24], heptane [13, 24], octane [11, 13], benzene [13, 16, 19, 26], toluene [11], methanol [10, 26], 1-propanol [11, 26], and 2-propanol [12, 25, 26].

Table 2 gives the maximal and mean errors in calculation from (1) for each combination relation for all the substances diffusing in the individual gases. The mean errors have been calculated without allowance for the calculated DC for heptane in the gases with $\sigma_i = 8.8 \times 10^{-10}$ m and $\varepsilon_i/k = 282.0$°K [4], since the markedly different results indicate that these values derived from the second virial coefficients are not suitable for forecasting the DC.

The open symbols in Fig. 1 denote the mean deviations, and the filled ones show the maximal ones, where we have used combinational rules (2)-(6). All the deviations are given in absolute magnitude. The symbols denote the following: minus all the calculated DC are overestimates; plus underestimates; plus-minus all deviations fluctuate about the mean value. Large discrepancies between the mean and maximal values show that (1) does not reflect the temperature dependence of the DC at atmospheric pressure with the corresponding parameters for the pure substances and the combinational rules.

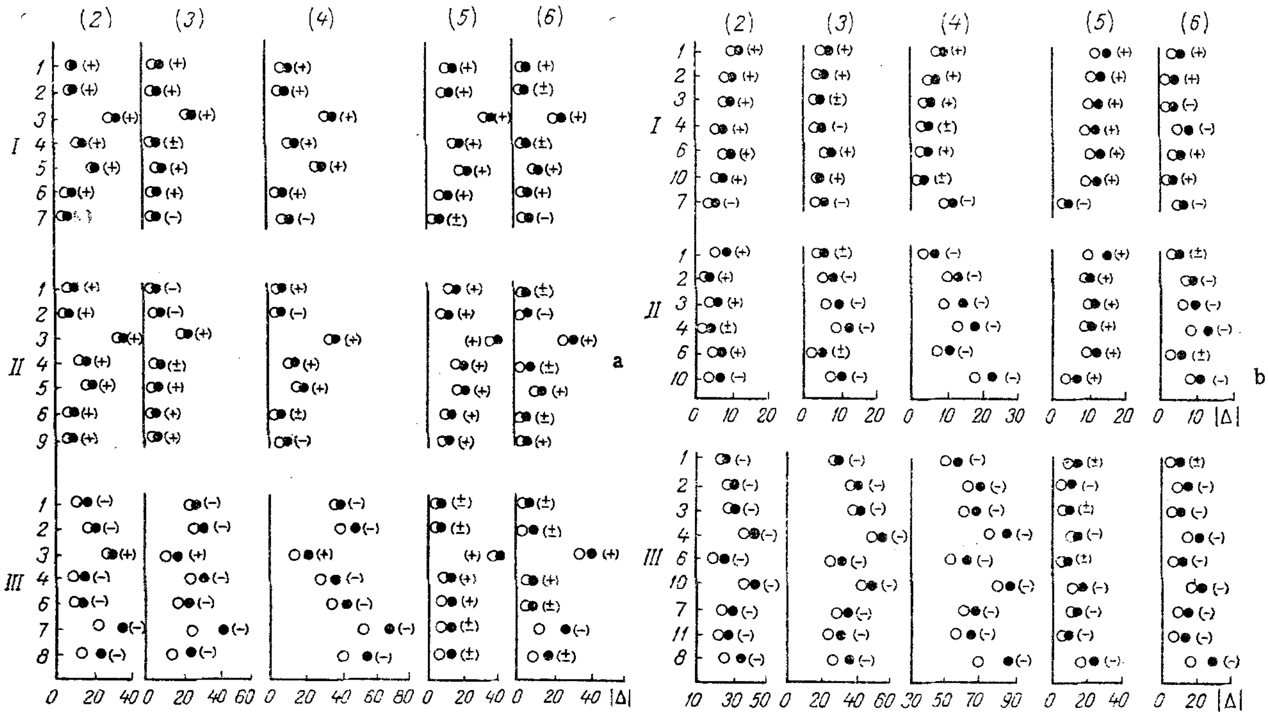

Fig. 1. Deviations in % of the observed diffusion coefficients for vapors of liquids in gases (carbon dioxide I, argon II, and helium III) from the results calculated from the kinetic-theory equation by different methods of combining the force parameters: a) 6-12 Lennard-Jones potential; b) Kessel'man effective potential (1, pentane; 2, hexane; 3, heptane; 4, octane; 5, nonane; 6, benzene; 7, 1-propanol; 8, methanol; 9, acetone; 10, toluene; 11, 2-propanol).

Table 2 and Fig. 1 indicate that: 1) one cannot give preference to any of these molecular-interaction potential models, 2) when one calculates DC for vapors in carbon dioxide, one can use the Kessel'man effective potential and combinational rules (6), while for argon one can use the 6-12 Lennard-Jones potential with (3) with σ_i and ε_i/k calculated from the viscosity, and 3) the largest deviations occur in systems containing helium. As the 6-12 Lennard-Jones potential enables one to select σ_{12} and ε_{12} [5, 11] such that one can fit the temperature dependence of the DC within the experimental error for binary mixtures involving either helium or carbon dioxide or argon, one assumes that these combinational rules are unsatisfactory. It is necessary to define new and better combinational rules for the parameters of the 6-12 Lennard-Jones potential.

NOTATION

D, D_t, experimental and calculated diffusion coefficients, m²/sec; T, temperature, °K; M_1, M_2, molecular masses of components 1 and 2, respectively; p, absolute pressure, hPa; σ_{12}, ε_{12}/k, parameters in the interaction potential for unlike molecules, m and K respectively; k, Boltzmann's constant, J/K; $\Omega_D = f(kT/\varepsilon_{12})$, reduced collision integral; Δ, deviation, %, and $\bar{\Delta}$, mean deviation, %, in (8); n, number of measured values for diffusion coefficient; j, current values of diffusion coefficient and deviation (j = 1, 2, ..., n); σ_i, ε_i/k, parameters of interaction potential for like molecules, m and K respectively (i = 1 for vapors, i = 2 for gases).

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