

MISCELLANEA

**INTERDIFFUSION COEFFICIENTS
IN ACTUAL GASEOUS SYSTEMS**

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UDC 533.15+546.21

Interdiffusion coefficients of ten gaseous pairs have been measured as functions of pressure at different temperatures. The measurements were performed by the two-bulb and stationary flow methods. The data obtained have been compared to the results of calculation from the formulas of rigorous and elementary kinetic theories. It has been shown that calculation from the formula obtained within the framework of the elementary kinetic theory is consistent with experiment within the experimental error.

Keywords: *gases, interdiffusion coefficient, experiment, molecular-kinetic theory.*

Introduction. Interdiffusion coefficients (ICs) are involved in many dimensionless heat- and mass-transfer numbers and are widely used for investigation of combustion processes, in chemical kinetics, and for calculation of the parameters of intermolecular interaction.

A certain amount experimental material on rarefied gases has been accumulated at present; kinetic diffusion theories satisfactorily describing this process in rarefied gases and making it possible to calculate the corresponding coefficients have been developed. However, a different situation arises with investigating diffusion in moderately dense and dense gaseous systems. Quite limited experimental data on this diffusion have been obtained thus far, mainly on diffusion in the low-temperature range.

Also, there is no reliable method or corresponding theory for calculation of the ICs of dense gases. The existing methods of description of the diffusion process at elevated pressures, such as the rigorous kinetic theory with its modifications, the dimer theory, and the phenomenological approach within the framework of nonequilibrium thermodynamics, make it impossible to describe the diffusion at elevated pressures within wide limits of variation in the parameters. Therefore, it becomes necessary to carry out experimental and theoretical investigations of the process of interdiffusion of dense gases.

To measure the ICs of gases one currently uses the Loschmidt and Stefan methods, the two-bulb method, the capillary, magnetic-resonance, and open-tube (elution) methods, the optical and dynamic methods, and the stationary flow method.

Measurement of the ICs of dense gases has a number of special features: the equipment employed should withstand pressure differences; the experimental time should be acceptable, since the IC decreases nearly in proportion to pressure, which, naturally, involves apparatuses of different geometry; certain difficulties are presented by an analysis of the composition of a mixture on diffusion; it is required that the mixing effects manifesting themselves as a change in the pressure in the diffusion device be taken into account.

We believe that the use of the stationary flow and two-bulb methods makes it possible to minimize and to even eliminate the influence of the above-enumerated factors on the results of measurement of the ICs of dense gases.

Experimental Setup and Measurement Procedure. To investigate gaseous diffusion at elevated pressures, one currently uses the two-bulb method [1, 2] in the main. The two-bulb device represents two vessels connected by a capillary: by a narrow tube. When the gas is injected and the gaseous mixture is analyzed, the bulbs are cut off from each other with shut-off devices. We used two such devices: one was equipped with a jacket making it possible to utilize a liquid heat-transfer agent which ensured a temperature of 250 to 400 K within the apparatus, whereas the

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TABLE 1. Geometric Parameters of Diffusion Apparatuses for IC Measurement by the Two-Bulb Method

Apparatus number	Bulbs		Capillaries	
	h_b and d_b , mm	V_b , cm ³	l_{cap} , mm	d_{cap} , mm
1	40.05	48.31	200.00	5.020
2	66.32	220.43	140.00	3.050
3	85.14	476.24	160.00	3.980

TABLE 2. Geometric Parameters of Diffusion Cells for IC Measurement by the Stationary Flow Method

Diffusion-cell number	Cells			Capillaries		
	l_c , mm	b_c , mm	$h_{sl.g}$, mm	S_t , cm ²	l_{cap} , mm	d_{cap} , mm
1	280.0	78.0	1.00	2.096	100.4	3.00
2	280.0	78.0	3.00	1.726	149.7	3.00

TABLE 3. Comparison of Gaseous ICs Measured by Different Methods

T , K	P , MPa	Two-bulb method		Stationary method		From [3, 5–7]	
		D_{12}^p , cm ² /s	Diffusion-apparatus number	D_{12}^p , cm ² /s	Diffusion-cell number	D_{12}^p , cm ² /s	Measurement method*
<i>Hydrogen-carbon dioxide (H_2-CO_2)</i>							
297	1.01	0.0628	1, 2, 3	0.0619	1, 2	0.0625	T
297	2.02	0.0305	2, 3	0.0300	1, 2	0.0307	F
297	4.05	0.0138	1, 2	0.0136	1, 2	0.0134	T
<i>Helium-carbon dioxide (He-CO_2)</i>							
303	1.00	0.0635	2, 3	0.0627	1, 2	0.0624	F
303	3.00	0.0188	2, 3	0.0184	1, 2	0.0186	T
303	5.00	0.00928	1, 2	0.00924	1, 2	0.00926	F
<i>Propane-carbon dioxide (C_3H_8-CO_2)</i>							
300	0.1	0.0080	1, 2, 3	0.0082	1, 2	0.0081	T
300	0.4	0.0078	1, 2	0.0079	1, 2	0.0077	T
300	0.6	0.0071	1, 2	0.0072	1, 2	0.0073	T

*T, two-bulb method, F, stationary flow method.

other had an electric heater and ensured experiments at a temperature of 350 to 800 K. Pressure in the system was continuously monitored by a reference manometer connected to it with a membrane separator. An analysis of the gaseous mixture on diffusion was made by the optical method using a Rayleigh interferometer with a 1-m-long gas cell or by the gravimetric method at atmospheric pressure. The gas pressure at the instant of analyzing was measured by the reference manometer of a calibration office accurate to 0.05 Mbar. We used three diffusion apparatuses with bulbs and capillaries of different geometry depending on experimental temperature and pressure. Instead of spherical bulbs traditionally used in such investigations, we used bulbs manufactured in the form of regular cylinders with a diameter of a cylinder equal to its height. As has been shown in [3], such replacement does not lead to a deviation of the results of measurement of the gaseous ICs, which is beyond the experimental error. The geometric dimensions of the cylinders were determined using a slide caliper with a scale value of 0.02 mm and a measuring microscope with a scale value of 0.005 mm. The geometric dimensions of the diffusion apparatuses used are given in Table 1.

Interdiffusion of gases is usually investigated by the stationary flow method. In our experiments, we used an apparatus making it possible to implement this method for dense gases [4]. Its basic element was a diffusion cell representing two slot channels connected by a set of capillaries. The angles of the diffuser and the confuser of the slot channels and the distance from the inlet of a slot channel to the capillary system were selected so as to ensure non-separating laminar gas flow in the cell. The capillaries were staggered. Two polished and calibrated cylinders, in which pistons set in motion by two rods were moving, served to create gas flow. The rods were fixed on a nut that travelled

TABLE 4. Experimental Data on the ICs of the Investigated Gaseous Pairs

No.	Gaseous system	ΔP , MPa	ΔT , K	Measurement method	Number of experimental values	Average deviation of calculation from experiment, %
1	H ₂ -CH ₄	0.1-6.0	260-500	Two-bulb, flow	32	2.1
2	H ₂ -C ₆ H ₆	0.1-3.0	400-500	Two-bulb	15	2.8
3	H ₂ -C ₃ H ₈	0.1-6.0	297-500	Two-bulb, flow	34	2.7
4	H ₂ -C ₂ H ₆	0.1-6.0	260-500	Two-bulb, flow	19	2.9
5	CH ₄ -C ₂ H ₆	0.1-6.0	260-500	Two-bulb, flow	59	3.0
6	CH ₄ - <i>n</i> C ₄ H ₁₀	0.01-0.5	273-498	Two-bulb, flow	49	3.2
7	N ₂ -C ₂ H ₆	0.1-6.0	260-500	Two-bulb, flow	32	2.8
8	C ₃ H ₈ -CO ₂	0.1-6.0	253-600	Two-bulb	41	2.4
9	H ₂ -CO ₂	0.1-6.0	260-500	Two-bulb, flow	44	2.2
10	O ₂ -CO ₂	0.1-6.0	280-600	Two-bulb	65	2.2
Total amount of experimental points					390	

over an engine-driven shaft. The shaft's rotational velocity could be varied within wide limits using a reducer. This made it possible to vary the volume velocity of a gas flow from 0.001 to 1.5 cm³/s. Manostats served to smooth possible pulsations of the gas flows. The reference manometer continuously monitored the system's pressure. A ballast tank served to equalize pressure in both cylinders. An analysis of the gaseous mixture was made with the optical and gravimetric methods of measurement of the gas concentration.

We conducted the experiments using two diffusion cells whose geometric dimensions are presented in Table 2. The basic mass of measurements was performed on cell No. 1. Thermostating of these cells was effected in the same manner as that for two-bulb apparatuses. Each cell was manufactured in two copies one of which was thermostatted using a liquid thermostat, and the other, using an electric heater.

The devices described enabled us to measure ICs at pressures of 0.01 to 6.0 MPa and temperatures of 253 to 600 K. We performed, on three devices, series of measurements of ICs with the aim of checking their effectiveness and the accuracy of experimental data obtained. The averaged results of 14-16 measurements of the IC of three gaseous systems are given in Table 3. This table also gives data obtained by other authors. The total error of measurements by the flow method amounted to 1-2% with reliability $\alpha = 0.95$, whereas that of measurements by the two-bulb method amounted to 2-3%. As is seen from the table, the results of IC measurement by the two indicated methods are consistent within the experimental error and agree well with the data of other authors.

Results of IC Measurement and Calculation. Using the devices described above we investigated experimentally the pressure (baric) dependence of the ICs of eight binary gaseous systems containing hydrocarbons, and also of the systems "carbon dioxide-hydrogen" and "carbon dioxide-oxygen" at different pressures. The list of the investigated gaseous systems, the ranges of their thermodynamic parameters, and the experimental data obtained are given in Table 4.

Earlier [8] we obtained, within the framework of the elementary kinetic theory, a formula making it possible to calculate the IC value at any temperature and pressure:

$$\overline{D}_{12}^P = \frac{D_{12}^0 P^0}{P} z_1 z_2 A, \quad (1)$$

where A is the dimensionless quantity defined as

$$A = \frac{c_1^P \sqrt{m_1 z_2} + c_2^P \sqrt{m_2 z_1}}{c_1^P z_2 + c_2^P z_1 \alpha_{12}^P} \sqrt{\frac{c_1 \sqrt{m_1} + c_2 \sqrt{m_2}}{c_1 + \alpha_{12} c_2}}, \quad \alpha_{12} = \left(\frac{\sigma_{11} + \sigma_{22}}{2\sigma_{11}} \right) \sqrt{\frac{m_1 + m_2}{2m_2}} \frac{1 - \omega_{12}}{1 - \omega_{11}}.$$

The expression for α_{12}^P has a form analogous to the expression for α_{12} , with $m_i z_i$ being involved in it instead of m_i .

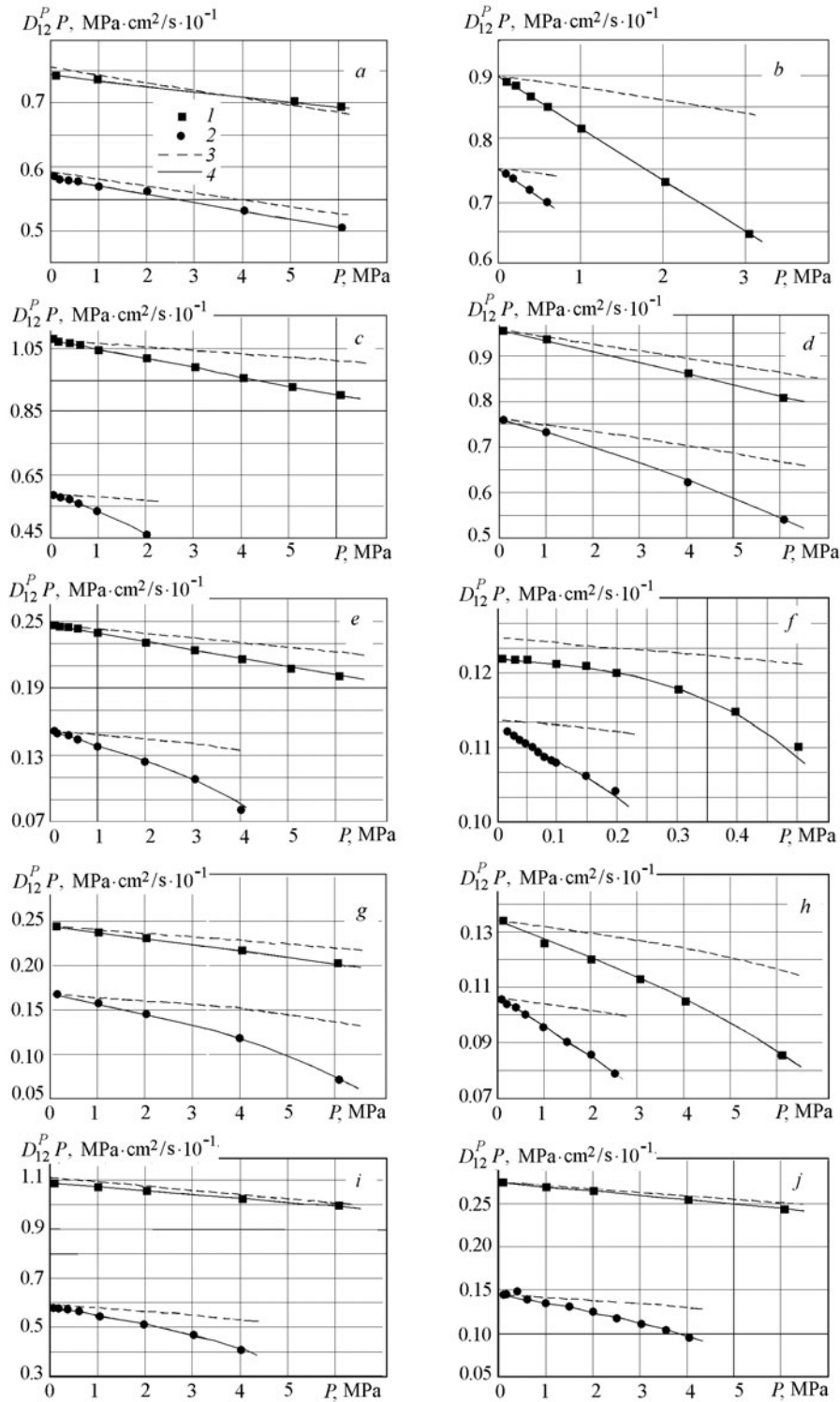


Fig. 1. Product D_{12}^P of the systems $\text{H}_2\text{-CH}_4$ (a), $\text{H}_2\text{-C}_6\text{H}_6$ (b), $\text{H}_2\text{-C}_3\text{H}_8$ (c), $\text{H}_2\text{-C}_2\text{H}_6$ (d), $\text{CH}_4\text{-C}_2\text{H}_6$ (e), $\text{CH}_4\text{-}n\text{C}_4\text{H}_{10}$ (f), $\text{N}_2\text{-C}_2\text{H}_6$ (g), $\text{C}_3\text{H}_8\text{-CO}_2$ (h), $\text{H}_2\text{-CO}_2$ (i), and $\text{O}_2\text{-CO}_2$ (j) vs. pressure at different temperatures: a) $T = 260$ and 300 , b) 450 and 500 , c) 350 and 500 , d) 350 and 400 , e) 300 and 400 , f) 298 and 348 , g) 320 and 400 , h) 350 and 400 , i) 280 and 400 , and j) 280 and 400 K; 1 and 2), experiment; 3) Enskog–Thorne theory; 4) calculation from formula (1).

TABLE 5. Comparison of Experimental ICS and ICs Calculated from Formula (1)

No.	Gaseous system	ΔP , MPa	ΔT , K	Average deviation of calculation from experiment, %	Reference
1	H ₂ -Ar	0.1-15.0	298, 363	2.1	[10]
		1.0-4.0	273-353		[11]
2	He-H ₂	1.0-4.0	273-353	2.7	[11]
		0.1-1.0	103-300		[12]
3	He-N ₂	1.0-4.0	273-353	3.2	[11]
		0.15-16.0	173-273		[13]
4	He-O ₂	0.1-1.0	103-300	3.8	[12]
		1.0-4.0	273-353		[11]
5	H ₂ O-H ₂	1.0-2.5	300, 323	4.8	[14]
		2.5-3.0	341, 15		[15]
6	He-CO ₂	1.0-2.5	321, 15	2.3	[3, 5]
		0.01-8.0	220-350		[6]
7	Ar-CO ₂	0.1-6.0	273-303	2.5	[14]
		1.0-2.5	230-400		[14]
8	N ₂ -CO ₂	1.0-10.0	323-353	4.6	[19]
9	C ₃ H ₈ -CO ₂	0.1-3.0	253-353	2.2	[6]
10	He-CH ₄	0.1-9.3	187-293	2.0	[13]
11	H ₂ -CO ₂	0.1-5.0	295	2.1	[7]
12	Ar-CH ₄	2.0-15.0	293	2.3	[16]
13	N ₂ -O ₂	1.0-2.5	300, 323	4.2	[17]
14	O ₂ -Ar	1.0-2.5	300, 323	4.1	[17]
15	CO ₂ -Kr	0.5-5.8	308	2.2	[18]

If an IC is measured with certain changes in the concentrations, relation (1) must be integrated with respect to concentration. When the change in the concentration is small (to 5%) the quantity A differs little from unity (1-2%), which substantially simplifies formula (1).

Figure 1 gives as an example the products D_{12}^P as functions of the pressure P for the gaseous pairs investigated at different temperatures; calculations from the formula of the Enskog-Thorne rigorous kinetic theory [9] and from formula (1) are given here, too. As is seen from the figure, the calculations from formula (1) are in good agreement with experiment. The calculations from the Enskog-Thorne formula yield substantial deviations from experiment. The average deviations of the ICs calculated from formula (1) from experimental values are given in the last column of Table 4. As is seen from this table, the deviations are mainly within the experimental error.

Also, we have compared experimental data on ICs obtained by other authors for 15 gaseous pairs. The results of such comparison are given in Table 5. As is seen from this table, the average deviation of the calculated data from experimental ones is no higher than 5% at different temperatures and pressures.

Unfortunately, most of the gaseous systems of Table 5 do not exhibit substantially their actual properties in the investigated range of thermodynamic parameters, except for the systems in which carbon dioxide is one component or for the investigations in the low-temperature range. Furthermore, the temperature dependence of the IC at different pressures has not been investigated, in practice, for most gaseous systems, except for the works of Karpushin [3, 5, 6, 12] and Dunlop [14]. Taking these drawbacks into account, we carried out a system investigation of gaseous systems in a wide range of temperatures and pressures.

The authors of publications given in Table 5 also point to the deviation of experimental data from those calculated from the Enskog-Thorne theory, except for systems of gases whose properties differ little from the properties of rarefied gases in the range of parameters used in the above investigations.

Conclusions. The performed comparative analysis of the obtained experimental data and the data of other authors and the results of IC calculations for 22 gaseous systems shows that the formula proposed for computation of an IC makes it possible to use this coefficient with an error of 2 to 5% throughout the parametric range of the systems investigated; also, this formula can be used for computation of the ICs of other actual gaseous systems.

NOTATION

b_c , width of a cell in the stationary flow apparatus, mm; c_i^P , relative volume-average concentration of the i th component; c_i , relative number concentration of the i th component; D_{12}^0 , interdiffusion coefficient at the pressure P^0 , cm^2/s ; D_{12}^P , interdiffusion coefficient at the pressure P , cm^2/s ; d_b , diameter of a bulb in the two-bulb apparatus, mm; d_{cap} , diameter of a capillary in the two-bulb apparatus or the stationary flow apparatus, mm; h_b , height of a bulb in the two-bulb apparatus, mm; $h_{\text{sl.g}}$, height of the slot gap of the cell in the stationary flow apparatus, mm; l_c , length of a cell in the stationary flow apparatus, mm; l_{cap} , length of a capillary in the two-bulb or stationary flow apparatus, mm; m_i , mass of an i molecule, kg; P , pressure, MPa; ΔP and ΔT , investigated ranges of pressures and temperatures; T , temperature, K; S_t , total area of capillaries in the stationary flow apparatus, cm^2 ; V_i , specific volume of the i th component, m^3 ; V_b , volume of a bulb in the two-bulb apparatus, cm^3 ; $z_i = PV/RT$, compressibility factor of the i th component; σ_{ij} , effective diameter of an i molecule, Å; ω_{11} and ω_{12} , persistence of molecular velocities for a pure gas and a gaseous mixture. Subscripts: c, cell; b, bulb; cap, capillary; sl.g, slot gap; t, total; 11, pure gas; 12, gaseous mixture; i , component number.

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