METHODS OF DETERMINING THE THERMAL-DIFFUSION CONSTANT IN LIQUID MIXTURES

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The article discusses methods for determining Soret coefficients in highly diluted solutions and liquid isotope mixtures.

The measurement of the thermal-diffusion constant (α_T) or the Soret coefficient (α_T/T) has two purposes: to verify various theories of transfer and to make clear the possibilities of using thermal diffusion as a technological separation process. The traditional method for the experimental determination of these quantities is the use of cells of various construction, which make it possible to record the value of the elementary thermal-diffusion effect, expressed by the formula

$$\Delta c = c_0(1 - c_0)\alpha_T \ln\frac{T_2}{T_1}. \tag{1}$$

It can be seen from (1) that for a sensitivity to concentrations of the order of $5 \cdot 10^{-6}$ in such mass-produced instruments as interferometers and chromatographs, a satisfactory measurement accuracy for readily separable mixtures ($\alpha_T \approx 1$) can be attained when one of the components has an initial concentration not less than several tenths of one percent. The use of interferometers, when $c \ll 1$, requires working with very pure substances, since in this case the effect of the impurities may be very significant. In order to eliminate this effect, chromatographs should be used. However, a sample for analysis must be taken from the cell, and sampling techniques do not guarantee that it will be representative. For isotope mixtures whose analysis is carried out by a mass-spectrometric method, the measurement error increases sharply as the concentration of one of the components of the binary mixture decreases, and if we take account of the small values of α_T for these mixtures (of the order of 10^{-2}), we see that reliable results can be obtained if the concentration shifts by 2-3%. Therefore it is practically impossible to determine α_T in the region of low concentrations of one of the components of a binary mixture (<1%) in the cells, and a great amount of experimental data published by various investigators is limited to values $c_0 > 2\%$ for various binary mixtures, while at the present state of measurement accuracy, cells generally are not used for liquid isotope mixtures.

However, from the data on the values of α_T obtained in the region of concentrations $c_0 > 2\%$ it does seem possible to determine the values of α_T when $c_0 \ll 1\%$. Let us give a few examples. In [1] it was shown that while in the region of medium concentrations in a mixture of benzene and carbon tetrachloride the Soret coefficient varies relatively little, it decreases sharply when the concentration of each of the components is of the order of 2%. In a mixture of benzene and ethanol [2] the curve showing the variation of α_T as a function of the benzene concentration is characterized not only by the presence of an extremum but also by a change in the sign of α_T. Analogous results were obtained for mixtures of methanol with carbon tetrachloride and ethanol with carbon tetrachloride [3]. These and a number of other investigations show that extrapolation of data to the region of low concentrations cannot yield the reliable values of α_T that are needed for solving the problem of using thermal diffusion as a technological process for purifying substances when the impurities are present in a concentration of the order of $c_0 \approx 10^{-3}$.

It therefore becomes necessary to develop methods which will make it possible to determine α_T in the region of low concentrations. In gaseous mixtures this problem can be solved relatively simply by using a swing separator [4], which makes it possible to increase the

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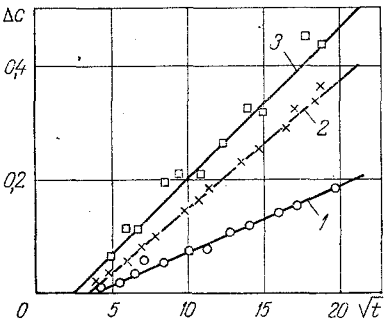

Fig. 1

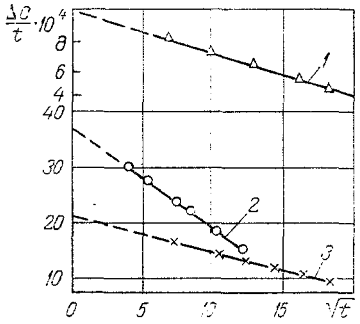

Fig. 2

Fig. 1. Δc as a function of $\sqrt{t}$, min $^{1/2}$, from the data of [12], for a mixture of benzene and n-heptane: 1, 2, 3) c_0 = 0.25, 0.5 and 0.75 mole fractions of benzene, respectively.

Fig. 2. Δc/t as a function of $\sqrt{t}$ for a mixture of benzene and n-heptane according to the data of [12]: 1, 2, 3) c_0 = 0.25, 0.5, and 0.75, respectively; $(\Delta c/t)\cdot 10^4$, min^{-1}.

elementary separation effect by about one order of magnitude, but for liquids this method cannot be used because the diffusion coefficient is very small. This difficulty can be overcome if we use a Clausius thermal-diffusion columns, in which the elementary thermal-diffusion effect in the horizontal direction is greatly magnified as a result of the vertical convective countercurrent motion caused by the horizontal temperature gradient. The theory of such a column, developed by the authors of [5], has been verified many times and found to be in excellent agreement with experimental data [6-9]. However, in order to achieve such agreement, great care must be taken in preparing the apparatus and ensuring a high degree of isothermality on both thermostated surfaces. Otherwise parasitic convective flows will occur in the thermal-diffusion column, reducing the separation effect. The harmful effect of the parasitic motion can be eliminated by various methods. One of these is to carry out the process in nonstationary conditions; here it must be borne in mind that, as we showed in [31], at the beginning of the separation process the effect of the parasitic convection is quite small: This becomes understandable if we consider the fact that the parasitic flow is smaller by almost two orders of magnitude than the convective flow providing a large amplification of the elementary effect.

The theoretical consideration of the transfer process is based on the solution of the nonlinear equation

$$\frac{\partial c}{\partial \theta}=\frac{\partial}{\partial y}\left[\frac{\partial c}{\partial y}-c(1-c)\right]. \tag{2}$$

If we take as our boundary conditions the vanishing of the flows at the ends of the column, as was done by the authors of [10], then on the initial segment of the kinetic curve giving the concentration as a function of time, we obtain the relation

$$\Delta c = 4c_0(1-c_0)\sqrt{\theta/\pi}, \tag{3}$$

in which Δc is the difference in concentration between the ends of the column. The expression (3) indicates that at time $\theta = 0$ we must have $\Delta c = 0$. However, as was shown by the authors of [11,12], in experiments with a mixture of benzene and heptane this condition is not maintained, and in the coordinates Δc and $\sqrt{t}$ the straight lines obtained by the method of least squares do not pass through the origin but intersect the positive abscissa axis (Fig. 1). We gave an explanation for this phenomenon in [13,14]: the boundary conditions must take account of the existence of mixed zones at the ends of the column; these zones are equivalent to several volumes, and taking account of them leads to the following formulation of the boundary conditions:

$$\begin{aligned} y_e\omega_i\left.\frac{\partial c}{\partial \theta}\right|_{y=0} &= \left[\frac{\partial c}{\partial y}-c(1-c)\right]_{y=0},\\ y_e\omega_e\left.\frac{\partial c}{\partial \theta}\right|_{y=y_e} &= \left[c(1-c)-\frac{\partial c}{\partial y}\right]_{y=y_e}. \end{aligned} \tag{4}$$

TABLE 1. Values of the Thermal-Diffusion Constant in a Heptane–Benzene Mixture, Obtained in Cells, and in a Thermal-Diffusion Column

Benzene concentration, ppm	Values of α_T			
	by formula (3) at 27 °C	from [16]	from [17]	by formula (8) at 27 °C
		at 25 °C		
0,25	0,42	0,865	0,99	0,99
0,50	0,69	1,32	1,48	1,34
0,75	1,07	1,69	1,96	1,77

Solving (2) with the conditions (4) and the linear approximation $c(1 - c) = a + bc$ yields the following asymptotic solution for small values of time [15]:

$$v_{e,i} = \pm\frac{1}{2k\pm 1}\left\{\pm 1 + \left[1 + \frac{(2k\mp 1)(4k^2+1)}{2(2k\pm 1)x}\right]\operatorname{erf}\frac{\sqrt{x}}{2k\mp 1} + \right.$$
$$\left. + \frac{2k(2k\mp 1)}{(2k\pm 1)x}\left[\exp\left(\frac{2k\pm 1}{2k\mp 1}x\right)\operatorname{erfc}\frac{2k\sqrt{x}}{2k\mp 1} - 1\right] + \frac{2k\mp 1}{\sqrt{\pi x}}\exp\left[-\frac{x}{(2k\mp 1)^2}\right]\right\}, \tag{5}$$

in which

$$v_{e,i} = \frac{b u_{e,i}(2k\mp 1)}{2c_0(1-c_0)x}, \quad x = \frac{\theta^*}{4}(2k\mp 1)^2, \quad k = \frac{1}{\overset{*}{y_e}\,\omega_{e,i}} \pm \frac{1}{2}, \tag{6}$$

with the upper signs referring to the positive end of the column for $b > 0$ and the negative for $b < 0$. The special feature of this solution consists in the fact that in the interval $0.01 < x < 0.3$ it can be approximated by the linear formula

$$\Delta c/t = h - n\sqrt{t} \tag{7}$$

with an error less than 1%.

From formula (7), taking account of (6) and the notation adopted here, we readily obtain a calculation formula for determining α_T:

$$\alpha_T\sqrt{D} = 0.308\,\frac{h^2\bar{T}\delta}{c_0(1-c_0)n\Delta T}, \tag{8}$$

in which h and n are, respectively, the interval cut off on the ordinate axis and the angular coefficient of a straight line constructed in the coordinates $\Delta c/t$ and $\sqrt{t}$.

The results obtained by processing the experimental data of the authors of [12] in this coordinate system are shown in Fig. 2, from which the values of h and n necessary for the calculation by formula (8) were found. The results of these calculations are shown in Table 1, which includes both the most reliable data on α_T obtained in cells [16,17] and the results of calculation by formula (3); the latter, as can be seen from Table 1, yields α_T values only about half as large. Table 1 also shows that the calculation by formula (8) and the data obtained in cells are in good agreement, to within 10%, while the α_T data in cells of different construction differ from one another by about the same amount. According to (8), in order to calculate α_T, we must know the value of the diffusion coefficient, which in the case of highly diluted solutions can be calculated by the Wilke–Chang formula.

An analysis of (5) shows that for small values of time the concentration at either end of the column is independent of its value at the opposite end. Therefore, there is no need to measure the concentration at both ends of the column, and we can get good results by making measurements at only one end. The calculation method is somewhat complicated by the fact that the angular coefficient on the approximating curve (7) becomes a function of the product ωy_e. The appropriate calculation method is described in [14].

The method described here is used for calculating the Soret coefficients of a series of binary mixtures [14], and the experimental apparatus used for this purpose is shown in Fig. 3. The coaxial cylinders between which the mixture to be separated was placed were manufactured with fairly high precision, as indicated by the data in Table 2. The working capacity of the method was verified by computing the results with analogous results obtained in cells (Table 3). It can be seen from the table that in most cases the Soret coefficient in the

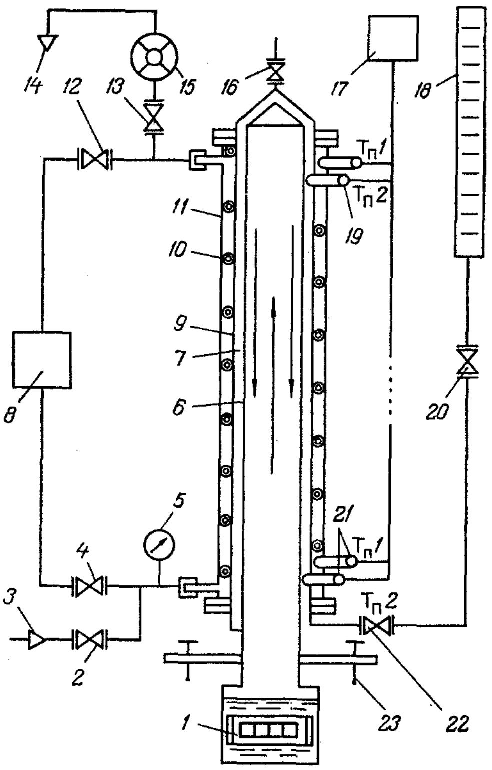

Fig. 3. Experimental apparatus for determining the Soret coefficient in a thermal-diffusion column: 1) steam generator with electric heater; 2, 4, 12, 13, 16, 20, 22) valves; 3) cooling-water input; 5) manometer; 6) inner cylinder; 7) working gap; 8) thermostat; 9) outer cylinder; 10) guiding spiral; 11) jacket of cooler; 14) water outlet; 15) water meter; 17) potentiometer; 18) burette to be filled; 19, 21) thermocouples; 23) adjusting screws.

column experiments is higher than the coefficient found in the cells, which is readily understandable if we take account of the fact that in the cells it is impossible to eliminate the mixing effects arising from the nonuniformity of the temperature field at the lateral surfaces of the cell, as was shown in [22]. The calculated error in the values of s in the column experiments was less than 10% in all cases.

This method was also used in [23] for determining the value of the thermal-diffusion constant α_T for bromine isotopes in a number of bromine compounds. The following results were obtained: butyl bromide, 0.40; amyl bromide, 0.035; heptyl bromide, 0.030. From these data it is clear that the values are to one another approximately as the relative mass differences.

Thus, the main advantages of the nonstationary method are the following: 1) shortening of the experiment time; 2) elimination of the effect of parasitic convection; 3) reduction of the error introduced as a result of inaccuracies in measuring the gap. In the stationary state $s \sim \delta^4$, whereas in the transition process $s \sim \delta$.

The smaller the relative error in the measurement of the gap, the more accurate the results obtained will be. From this point of view, columns with packing have the advantage that they make it possible to work with δ values higher than those of columns without packing by almost one order of magnitude. Furthermore, in packed columns there is practically no parasitic-convection effect [19]. In packed columns there is a sharp increase in the time required for the transition process, which makes it necessary to carry out precision measurements of the changes in concentration in experiments with isotope mixtures. With this type of column, we used a nonstationary method in [32] to determine the reduced value of the thermal-diffusion constant for chlorine isotopes in carbon tetrachloride constituting a

TABLE 2. Geometric Characteristics of the Thermal-Diffusion Column

Dist. from outer ring of external cylinder, mm	Average value, mm	
	interior diam. of external cylinder, mm	external diam. of internal cylinder
8	49,970±0,0025	—
100	49,972±0,0025	49,421±0,0020
150	49,968±0,0025	49,422±0,0020
250	49,975±0,0025	49,426±0,0020
300	49,976±0,0025	49,421±0,0020
387	49,976±0,0025	—

multicomponent mixture. We found a value of $\alpha_0 = 3.4 \pm 0.7$. A disadvantage of the nonstationary method is the need for exact measurements of concentration changes, although the precision of these measurements can be much higher than in the case of cells.

In the cases in which the concentration changes are so small as to make it impossible to use the nonstationary method (this happens in a number of liquid isotope mixtures), the only alternative is a stationary method. However, in this case the effect of parasitic convection becomes serious, and the problem of taking account of this negative factor must be dealt with. We followed the course of using a comparative method consisting essentially in conducting the first experiment with a standard substance for which the value of the thermal-diffusion constant is known; from this, using the curve of Fig. 4, it is possible to find the parasitic-convection parameter

$$\varkappa y_e = 7560\left[\frac{\eta DL\,(\delta T)}{g\beta\rho\delta^4\,(\Delta T)^2}\right]_1, \tag{9}$$

which, as can be seen from the formula, depends on the physical characteristics of the mixture, the geometry of the column, and the temperature conditions of the experiment [24]. If in the same column we conduct an experiment with the mixture under investigation, we find for this mixture

$$\frac{(\varkappa y_e)_2}{(\varkappa y_e)_1} = \left(\frac{\eta D}{\beta\rho}\right)_2 \left(\frac{\beta\rho}{\eta D}\right)_1 \left[\frac{(\Delta T)_1}{(\Delta T)_2}\right]^2. \tag{10}$$

From the value found for $(\varkappa y_e)_2$ and from Fig. 4, we can determine the degree of separation that would exist if there were no parasitic convection, and then, using the formula

$$\alpha_T = \frac{g\rho\beta\delta^4\overline{T}\ln q^*}{504\eta DL}. \tag{11}$$

we can find α_T. Naturally, this method is not very accurate, since it is based on Fig. 4, which was obtained from model representations of the mechanism of parasitic convection in

TABLE 3. Comparison of Soret Coefficients Obtained by the Nonstationary Method in a Thermal-Diffusion Column and Those Obtained in Cells

Mixture	Concentration of first component, ppm	Soret coefficient, $s \cdot 10^3$ deg^{-1}	
		in column at $T=308$ °K	in cells at $T=298$ °K
$CCl_4—C_6H_{12}$	0,9648	6,6	—
	0,9885	—	7,25 [18]
	0,9010	—	6,13 [18]
$CCl_4—C_6H_6$	0,9578	7,4	5,65 [19]
$n\text{-}C_7H_{16}—C_6H_6$	0,9080	2,2	(flow-through cell)
	0,9000	—	2,3 [16] (308 °K)
	0,8995	—	2,87 [17] (308 °K)
$C_6H_6\text{-}n\text{-}C_6H_{14}$	0,9780	7,6	7,65 [20]
	0,9000		7,22 [20]
$n\text{-}C_{16}—H_{34}\text{-}n\text{-}C_7H_{16}$	0,9520	2,91	2,45 [21]
	0,8997		(membrane cell)

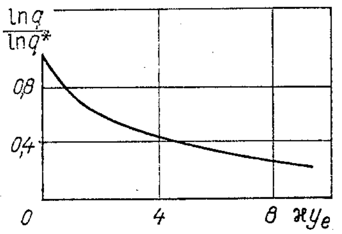

Fig. 4. Variation of the ratio (ln q)/(ln q*) as a function of the parameter $\varkappa y_e$.

columns and presupposes that when one liquid is replaced with another, the temperature asymmetry remains unchanged. This method was used for determining the value of the thermal-diffusion constant in a number of isotope mixtures [25,26]. The results are shown in Table 4. It is interesting to note that for sulfur isotopes in carbon disulfide Rutherford [27] (Mound Laboratory, United States) obtained a value of α_0 = 4.9, in other words, close to the value given in the table.

Theoretical study of the effect of parasitic convection on the process of separation of binary mixtures in a thermal-diffusion column operating in a sampling regime showed that under these conditions the convection decreases sharply [28]. This justified the use of the given result for determining the Soret coefficient. For large samples the calculation formula for obtaining this coefficient has the form

$$s = 6!\,\frac{\eta}{g\rho^2\beta\,(\Delta T)^2\,\delta^3 B}\;\frac{c_e - c_i}{[c_0^2 + (1 - 2c_0)\,c_i]\,\sigma_i + [c_0^2 + (1 - 2c_0)\,c_e]\,\sigma_e}. \tag{12}$$

As our working mixture, we took a water—ethanol mixture, containing a nearly azeotropic amount of alcohol: c_0 = 0.94. The values of s obtained are shown in Table 5 for various sample values [29].

The method described can be used only in cases when the mixture being separated is available in fairly large quantities.

In conclusion, we should mention the development of a method for calculating the thermal-diffusion constant in liquid isotope mixtures which has been proposed by B. N. Zamskii and is based on the methods of statistical mechanics. The special feature of the method is that the formula obtained for the reduced value of the thermal-diffusion constant, including such characteristics of an isotope mixture as the radial distribution functions and interaction potentials, was found to be expressible in terms of macroscopic properties, and the calculation formula for molecules with spherical symmetry has a simple form:

TABLE 4. Values of the Reduced Thermal-Diffusion Constants of Some Multicomponent Isotope Mixtures

Element	Compound	Reduced thermal diffusion constant α_0	Standard
Sulfur	C_4H_4S	4,4	C_6H_5Br
Titanium	$TiCl_4$	3,3	C_6H_5Br
Tin	$SnCl_4$	2,8	C_4H_9Br

TABLE 5. Values of the Soret Coefficient in an Ethanol—Water Mixture with c_0 = 0.94 and $\bar{T}$ = 310°K, Obtained from the Results of Operation with a Column in a Sampling Regime

Sample $\cdot 10^4$, g/sec		Conc., mole fractions ethanol		Soret coefficient, $s \cdot 10^3$ deg^{-1}
top σ_e	bottom σ_i	top	bottom	
4,6	4,68	0,959	0,928	—3,0
3,71	3,77	0,964	0,926	—3,2
1,75	1,80	0,983	0,885	—3,1

TABLE 6. Comparison of Experimental Data with Calculations Using Formula (13)

Element	Content	$\overline{T}$, °C	α_0	
			theory	experiment
	Spherical molecules			
Chlorine	CCl_4	53,5	3,4	3,4±0,7 [32]
	UF_6	114,5 156,5	2,7 1,7	2,6±0,8* 1,9±0,4*
	Asymmetric			
Hydrogen	$C_6D_6 + C_6H_6$	50,5	2,16	2,02†
	$C_6D_6 + C_6H_6$	83,5	1,89	2,02 [27]
	$C_6D_6 + C_6H_6$	96,0	1,75	2,42 [27]
	$C_6D_{12} - C_6H_{12}$	83,0	2,70	3,75 [27]
Carbon	$^{13}C^{12}C_5H_6 + ^{12}C_6H_6$	83,5	3,60	2,36 [27]
	$^{13}C^{12}C_5H_6 + ^{12}C_6H_6$	96,0	3,46	3,83 [27]
	$^{13}C^{12}C_5H_{12} + ^{12}C_6H_{12}$	83,0	2,53	2,87 [27]
Sulfur	$C^{32}S_2 + C^{32}S^{34}S$	96,0	3,24	4,80 [27]
Bromine	$C_6H_5{}^{79}Br + C_6H_5{}^{81}Br$	40,0	8,85	7,07 [35]

*Obtained by means of the calculation carried out in [33], using the experimental results of [34].

†Obtained by Rutherford [37] by recomputation of Korsching's experimental data [36].

$$\alpha_0 = \frac{1}{3}\left(\frac{V}{R}\frac{\beta}{\beta'} - 1\right). \tag{13}$$

In order to use this formula, we must know the coefficients of isothermal compression and volumetric expansion of the liquid, where the first of these can be calculated by using a relation proposed by Filippov [30]:

$$\frac{RT}{V}\beta' = 72\left(\frac{\rho_{cr}}{\rho}\right)^{7.5}. \tag{14}$$

Formula (13) was verified on the basis of the experimental data available in the literature concerning the values of the thermal-diffusion constants of binary isotope mixtures with molecules having spherical and nonspherical symmetry. The results of this verification are given in Table 6, for which it can be seen that the agreement between theory and experiment, taking account of the complexity of the description of the transfer phenomena by mechanical-statistical methods, is satisfactory.

NOTATION

c, concentration; α_T, thermal-diffusion constant; $\alpha_0 = \alpha_{ij}(M_i + M_j)/(M_i - M_j)$, reduced thermal-diffusion constant in a multicomponent mixture; M_i, molecular mass of component i; T_2, T_1, temperatures, $T_2 > T_1$; $\theta = H^2t/mK$, dimensionless time; t, time; $H = \alpha_T\rho^2 g\beta\delta^3(\Delta T)^2B/6!\eta\overline{T}$; ρ, β, η, density and coefficients of volumetric expansion and dynamic viscosity; $\Delta T = T_2 - T_1$; B, perimeter of the working gap; $\overline{T} = \frac{1}{2}(T_1 + T_2)$; δ, magnitude of the gap; D, diffusion coefficient; $K = g^2\rho^3\beta^2\delta^7(\Delta T)^2B/9!\eta^2D$; z, vertical coordinate; $y = Hz/K$; L, height of column; $y_e = HL/K$; $M_{e,\ i}$, mass of liquid in reservoirs at the top and bottom of the column; $m = B\rho\delta$; $\omega_{e,\ i} = M_{e,\ i}/mL$; $u_{e,\ i} = c_{e,\ i} - c_0$; $\theta^* = b^2\theta$; $y_e^* = by_e$; (δT), temperature asymmetry; $\varkappa$, dimensionless parasitic flow; q, degree of separation; q^*, degree of separation in the stationary state and no-sampling conditions, with no parasitic convection; $s = \alpha_T/T$, Soret coefficient; β', coefficient of isothermal compression; V, mole volume; ρ_{cr}, critical density; σ, sample. Subscripts: 0, initial value; e, i, positive and negative ends of the column, respectively.

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ON THE CALCULATION OF THE BARODIFFUSION CONSTANTS OF BINARY GAS MIXTURES (McCORMACK MODEL)

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An expression for the barodiffusion constant is obtained on the basis of the McCormack model equations in the approximation of a continuous medium.

The barodiffusion constant is an important physical quantity characterizing such phenomena as diffusiophoresis, separation of a mixture during flow, etc. Expressions for it are obtained in a number of reports using the Boltzmann equation [1,2] or model kinetic equations in the Hamel form [3,4]. When the values of the barodiffusion constant obtained from the solution of equations in the Hamel form are compared with experimental data [5,6] it turns out that they differ rather considerably from each other for a number of binary mixtures. The most important disagreement is observed for binary mixtures with molecules of markedly differing masses (Ar—H_2, Ar—He, Ar—Ne, etc.). Evidently, the reason for the noncorrespondence between the theoretical results and experimental data consists in the fact that the Hamel model does not describe sufficiently correctly the flow of a binary mixture in the mode of a continuous medium; in particular, an adequate description of the diffusion and viscosity of the mixture cannot be provided simultaneously within its framework. Thus, the necessity arises of using more refined models of a binary gas mixture. Such models include McCormack's model [7]. It is based on matching the moments of order N from exact and model collision integrals and provides a correct description of the flow of a mixture in the mode of a continuous medium. In [8] the method of half-space moments is used to solve model equations in the McCormack form with N = 2. Usually when this method is used difficulties develop in estimating the accuracy of the results obtained. Since even the second approximation of the method of half-space moments leads to very cumbersome expressions, it is practically impossible to find the third approximation, which would permit an estimation of the rate of convergence of the results obtained to numerical results. In the present report the method of asymptotic joining, which is free of the defects inherent to the method of half-space moments, is used to solve model equations in the McCormack form.

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