CALCULATION OF NONEQUIMOLAR DIFFUSION IN MULTICOMPONENT MIXTURES

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The article considers nonequimolar diffusion in multicomponent mixtures. An exact solution for the profile of instantaneous concentrations and an approximation to the flows of diffusing components are obtained.

The study of diffusion and mass transfer in multicomponent mixtures is necessary for the further improvement of such widely used processes as rectification, absorption, extraction, etc.

In the study of multicomponent diffusion the cases most commonly considered are those of equimolar diffusion [1-10] and diffusion in the presence of an inert substance [11, 12]. Subject to certain assumptions, the process of rectification may be considered on the basis of equimolar diffusion, and the process of absorption with a gaseous carrier not soluble in the absorbent, or with an absorbent which is not very volatile can be considered on the basis of diffusion in the presence of an inert substance.

In most processes, however, the mass transfer is nonequimolar, and consequently so is the diffusion; therefore the solution of the problem of nonequimolar transfer in multicomponent mixtures is of great importance not only from the scientific but also from the practical point of view.

The purpose of the present paper is to analyze the exact and approximate solution of the equation of nonequimolar diffusion and estimate the accuracy of the resulting approximate expressions and the range of their possible application.

The process of isothermal diffusion in (q + 1)-component gas and liquid mixtures is considered today to be describable by the following system of differential equations [13]:

$$-\nabla\mu_i = \sum_{j\neq i}^{q+1} F_{ij}C_j(v_i - v_j),\quad i = 1,\ 2,\ \ldots,\ q+1. \tag{1}$$

The equation used for an ideal gas mixture is the Stefan–Maxwell equation [14]

$$-C\nabla y_i = \sum_{j\neq i}^{q+1} \frac{N_i y_j - N_j y_i}{\mathcal{D}_{ij}},\quad i = 1,\ 2,\ \ldots,\ q+1. \tag{2}$$

On the basis of the above equation, we can obtain an approximate solution for flows of such mixtures; an exact solution for the concentration profile can be obtained only in the case of ideal gas mixtures.

The obvious constraints on the concentrations

$$\sum_{1}^{q+1} y_i = 1\ \left(\sum_{1}^{q+1}\nabla y_i = 0\right) \tag{3}$$

leads to the necessity of using additional relations concerning the flows in order to make the systems of equations (1) and (2) linearly independent.

The additional relations are usually determined by the conditions of equimolar diffusion ($\sum_{1}^{q+1} N_i = 0$)

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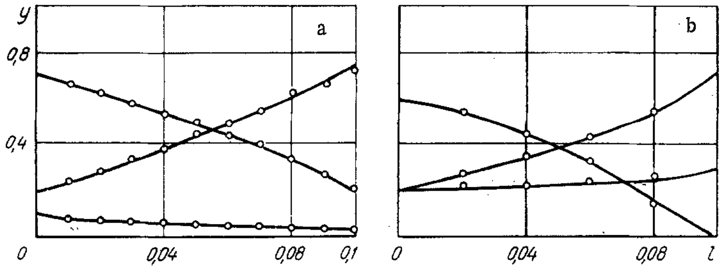

Fig. 1. Variation of the concentrations of the diffusing components along the diffusion distance.

or diffusion with an inert subtance ($N_{q+1} = 0$).

For conditions of nonequimolar diffusion — i.e., in the general case — we take the given relation between the flow of the (q + 1)-th component and the sum of all other components:

$$\frac{N_{q+1}}{\sum\limits_{1}^{q} N_i} = z, \tag{4}$$

which in the special cases z = −1 and z = 0 leads to the conditions of equimolar diffusion and diffusion with an inert substance, respectively.

In view of the constraints concerning the concentrations and the flows, Eq. (2) takes the following form:

$$-C\nabla y_i = \sum_{j \neq i}^{q} N_i\, y_j \beta_{ij} - \sum_{j \neq i}^{q} N_j y_i \gamma_{ij} + N_i \alpha_{i,\,q+1};\ i = 1,\ 2,\ \ldots,\ q, \tag{5}$$

where

$$\begin{gathered} \alpha_{ij} = \frac{1}{\mathcal{D}_{ij}}; \\ \beta_{ij} = \alpha_{ij} - \alpha_{i,q+1}; \\ \gamma_{ij} = \alpha_{ij} + z\alpha_{i,q+1}. \end{gathered} \tag{5a}$$

TABLE 1. Reference Systems for Determining Diffusion Flows

System	Weighting coefficient for average velocity, a_i	Average velocity, $v^a = \sum\limits_{i=1}^{q+1} a_i v_i$	Diffusion flow, $J_i^a = C_i (v_i - v^a)$	Additional condition on flows, $\sum\limits_{i=1}^{q+1} \frac{a_i}{C_i} J_i^a = 0$
Mass	Mass fraction m_i	Average mass velocity $v^m = \sum\limits_{1}^{q+1} m_i v_i$	$J_i^m = C_i (v_i - v^m)$	$\sum\limits_{i=1}^{q+1} \frac{m_i}{C_i} J_i^m = 0$
Mole	Mole fraction y_i	Average mole velocity $v^y = \sum\limits_{1}^{q+1} x_i v_i$	$J_i^y = C_i (v_i - v^y)$	$\sum\limits_{i=1}^{q+1} \frac{x_i}{C_i} J_i^y = 0$
Volume	Volume fraction $C_i \overline{V}_i$	Average volume velocity $v^V = \sum\limits_{1}^{q+1} C_i \overline{V}_i v_i$	$J_i^V = C_i (v_i - v^V)$	$\sum\limits_{i=1}^{q+1} \overline{V}_i J_i^V = 0$
Inert substance (solvent)	Kronecker delta $\delta_{i,q+1}$	Velocity of inert substance $v^0 = \sum\limits_{1}^{q+1} \delta_{i,q+1} v_i$	$J_i^0 = C_i (v_i - v^0)$	$J_{q+1}^0 = 0$
Laboratory	—	$v^z = -\sum\limits_{i=1}^{q} \sum\limits_{j=1}^{q} \overline{D}_{ij} \times$ $\times \Delta y_j (1 + z)$	$J_i^z = C_i (v_i - v^z)$	$\frac{N_{q+1}}{\sum\limits_{i=1}^{q} N_i} = z$

TABLE 2. Determination of Flows of Diffusing Components according to Eqs. (2) and (11)

No. of variant	z	$\mathcal{D}_{12}$	$\mathcal{D}_{13}$	$\mathcal{D}_{23}$	y_1^0	y_2^0	y_3^0	l	y_1	y_2	y_3	$N_1^{(2)}$	$N_1^{(11)}$	$N_2^{(2)}$	$N_2^{(11)}$	$N_3^{(2)}$	$N_3^{(11)}$
1	—1,0	1	5	3	0,1	0,2	0,7	0,1	0,5046	0,3757	0,1197	—10,95	10,89	—6,35	—6,46	17,3	17,35
2	—1,0	1	5	3	0,1	0,2	0,7	0,02	0,0076	0,1744	0,8186	10,95	10,95	6,35	6,37	—17,3	—17,32
3	—1,0	1	5	3	0,9	0,05	0,05	0,005	0,9139	0,0127	0,0733	10,95	11,03	6,35	6,37	—17,3	—17,4
4	—1,0	5	1	3	0,1	0,2	0,7	0,005	0,03746	0,1848	0,7778	10,95	10,97	6,35	6,35	—17,3	—17,32
5	—3,0	1	5	3	0,1	0,2	0,7	0,1	0,4503	0,1998	0,3499	—5,774	—5,74	0,0	0,002	17,3	17,25
6	19,03	1	45	3	0,1	0,2	0,7	0,1	0,0816	0,3466	0,5715	0,576	0,562	0,0	0,0	10,95	10,7
7	0,0	1	5	3	0,1	0,2	0,7	0,01	0,0071	0,2795	0,7134	17,876	17,877	—6,35	—6,35	0,0	0,0
8	—3,0	1	5	3	0,1	0,2	0,7	0,1	0,0331	0,7654	0,2015	0,576	0,57	—6,35	—6,22	17,3	16,96
9	—3,0	1	5	3	0,9	0,05	0,05	0,01	0,8661	0,1311	0,0028	0,576	0,583	—6,35	—6,36	17,3	17,3
10	—3,0	1	45	3	0,1	0,2	0,7	0,1	0,01976	0,7591	0,2211	0,576	0,548	—6,35	—6,21	17,3	17,0

Note. $N_1^{(2)}$, $N_2^{(2)}$, and $N_3^{(2)}$ are the flows determined from Eq. (11); $N_i \cdot 10^5$, g • mole/sec • cm^2; y_i^0 and y_i are given in mole fractions; $\mathcal{D}$, cm^2/sec; l, cm.

We can write Eq. (5) in matrix form:

$$-C(\nabla y) = {}^{\ulcorner}N_{\lrcorner}[\beta](y) - {}^{\ulcorner}y_{\lrcorner}[\gamma](N) + {}^{\ulcorner}N_{\lrcorner}(\alpha_{q+1}). \qquad (6)$$

Writing $[\gamma](N) = (w)$ and noting that ${}^{\ulcorner}y_{\lrcorner}(w) = {}^{\ulcorner}w_{\lrcorner}(y)$, we can transform Eq. (6) to the form

$$-C(\nabla y) = {}^{\ulcorner}N_{\lrcorner}[\beta](y) - {}^{\ulcorner}w_{\lrcorner}(y) + {}^{\ulcorner}N_{\lrcorner}(\alpha_{q+1}). \qquad (7)$$

Integration of the last equation along the diffusion distance leads to the following expression for the instantaneous concentrations of the diffusing components:

$$(y) = \exp\{-Cl[A]\}[(y_0) + [A]^{-1}(b)] - [A]^{-1}(b), \qquad (8)$$

where

$$[A] = {}^{\ulcorner}N_{\lrcorner}[\beta] - {}^{\ulcorner}w_{\lrcorner} \text{ and } (b) = {}^{\ulcorner}N_{\lrcorner}(\alpha_{q+1}). \qquad (8a)$$

An analysis of the profiles of instantaneous concentrations, calculated from Eq. (8) for diffusion in three-component, four-component, and five-component mixtures containing components with sharply differing physical properties, has shown that the law governing the concentrations of the diffusing components along the diffusion distance is nearly linear. Figures 1a and 1b show the characteristic curves of variation of the concentrations as functions of the diffusion distance for a three-component mixture. The initial data for the concentration profile shown in Fig. 1b are taken from [15] as an example of maximum observed nonlinearity in the concentration curves, but even in this case the linearity assumption is valid for a short diffusion distance.

The total mass flow (diffusive and convective) is determined by the "generalized Fick law," or by the phenomenological equation from the thermodynamics of reversible processes [16-18],

$$N_i = -C\sum_{j=1}^{q+1} D_{ij}\nabla y_j + N_t y_i, \qquad i = 1, 2, \ldots, q+1, \qquad (9)$$

where

$$N_t = \sum_{1}^{q+1} N_i. \qquad (9a)$$

Solving the system of equations (9), where the constraints on the concentrations (3) and the additional conditions on the flows (4) have been taken into consideration, we obtain

$$N_i = C\sum_{j=1}^{q}\left[D_{i,q+1} - D_{ij} + \frac{(1+z)(D_{q+1,j} - D_{q+1,q+1})y_i}{(1+z)y_{q+1} - z}\right]\nabla y_j, \qquad (10)$$

$$i = 1, 2, \ldots, q.$$

Taking the expression in square brackets as the proportionality constant $\bar{D}_{ij} = \bar{D}_{ij}(D_{ij}, y_i, z)$, we can write Eq. (10) in the form of a function analogous to the expression for the flow of a substance under conditions of equimolar diffusion:

$$N_i = -C\sum_{j=1}^{q} \bar{D}_{ij}\nabla y_j, \qquad i = 1, 2, \ldots, q. \qquad (11)$$

Let us consider, furthermore, how the proportionality constant $\bar{D}_{ij}$ in Eq. (11) varies as a function of the composition of the mixture and of the binary diffusion coefficients. Taking account of the transformations used by Toor [19] for equimolar diffusion, we can write Eq. (6) in the form

$$-C(\nabla y) = [\ulcorner u \lrcorner - \ulcorner y \lrcorner [\gamma] + \ulcorner \alpha_{q+1} \lrcorner (N), \tag{12}$$

where

$$(u) = [\beta]\,(y). \tag{12a}$$

Comparing (12) with Eq. (11), we obtain the following expression for the "practical" diffusion coefficients:

$$[\bar{D}]^{-1} = \ulcorner u \lrcorner + \ulcorner \alpha_{q+1} \lrcorner - \ulcorner y \lrcorner [\gamma], \tag{13}$$

and accordingly

$$\bar{D}_{ii}^{-1} = \sum_{\substack{j=1 \\ j \neq i}}^{q+1} \frac{y_j}{\mathcal{D}_{ij}} - z\,\frac{y_i}{\mathcal{D}_{i,q+1}} \tag{13a}$$

and

$$\bar{D}_{ij}^{-1} = -y_i \left(\frac{1}{\mathcal{D}_{ij}} + \frac{z}{\mathcal{D}_{i,q+1}} \right). \tag{13b}$$

It is readily seen that in the case of equimolar diffusion ($z = -1$) Eqs. (13) take the form of the equations used by Toor [19], and in the case of diffusion with an inert substance ($z = 0$) they become the expressions used by Frank—Kamenetskii [12].

The resulting solutions of the equations of nonequimolar diffusion (11), (13) enable us to state in explicit form the conditions for diffusion in the laboratory reference system [12, 20]. Table 1 shows the expressions for the diffusion streams and the average velocities of the diffusing components for various reference systems, including the laboratory system. As can be seen from the table, for all systems except the laboratory system the initial conditions taken are the average velocities, on the basis of which we have obtained expressions for the relation between the flows, while for the laboratory reference system the assumed conditions for the flow determine the average diffusion velocity.

In general the choice of a particular reference system depends, as is known, on the convenience and simplicity of the solution of a specific physical problem. The use of the above-cited relations for the laboratory reference system makes it possible to consider nonequimolar diffusion under conditions of given relations between the flows, for example, in a process with a chemical reaction when the amount of substance transferred is determined by stoichiometric coefficients, or in which the relation between the flows has been found experimentally.

It should be noted that the physical meaning of the reference system consists precisely in the additional conditions needed for solving the equations of multicomponent diffusion for the mass flows of diffusing components.

In the integration of Eq. (1) it is assumed that the practical diffusion coefficients are independent of the diffusion distance [21, 5, 6, 8], i.e., the equation is linearized.

The correctness of the assumed "linearized" theory under conditions of nonequimolar diffusion has been verified by comparing the results of calculations for flows with three-component, four-component, and five-component ideal gas mixtures in accordance with (2) and (11). The values of the elements of the inverse matrix of practical diffusion coefficients were determined from the arithmetic means of the concentrations of the diffusing components.

The calculations were carried out as follows. For the given values of flows and initial concentrations, in accordance with (2), the final compositions of diffusing components for the corresponding diffusion distance were calculated on the "Nairi" computer, using a standard program of numerical integration of a system of linear differential equations by the Runge—Kutta method with an integration interval of 0.01 cm. After that, on the basis of the given and calculated compositions, the flows N_i were determined in accordance with (11).

Table 2 shows the initial data and calculation results for ten characteristic variants of the diffusion. A comparison of the calculation results shows the applicability of the assumed "linearized" theory of multicomponent diffusion and the possibility of using the phenomenological equation (11) for describing the general case of diffusion, taking account of convective flow.

In view of the approximate nature of the solution proposed in this paper for the equations of nonequimolar diffusion, the values of z used should be checked on the basis of the requirements of thermodynamic stability of the system, which are formulated from the thermodynamics of irreversible processes [22-24].

NOTATION

C	is the total concentration of components in mixture, g·mole/cm^3.
C_i	is the concentration of component i, g·mole/cm^3;
D_{ij}	is the diffusion coefficient of multicomponent mixture;
$\bar{D}_{ij}^{-1}$	is the element of the inverse matrix of practical diffusion coefficient;
$\bar{D}_{ij}$	is the practical diffusion coefficient;
$\mathcal{D}_{ij}$	is the diffusion coefficient of binary mixture;
F_{ij}	is the coefficient of friction;
J_i	is the diffusion flow of component i relative to the given reference system;
l	is the diffusion distance;
N_i	is the flow of component i relative to fixed reference system;
y_i	is the concentration of component i in vapor phase, g·mole/g·mole;
y_i^0	is the initial concentration of component i in vapor phase, g·mole/g·mole;
v	is the average velocity of mixture;
$\bar{V}_i$	is the partial molar volume of component i;
ΔY	is the difference in concentration;
∇	is the gradient;
$[\ ]$	is the square matrix of order q;
$\ulcorner\ \lrcorner$	is the diagonal matrix of order q;
$(\ )$	is the column matrix of order q;
i, j	are the components (i, j = 1, 2, . . . , q + 1);
i, j	are the row and column of matrix (i, j = 1, 2, . . . , q).

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