APPROXIMATE MASS-TRANSFER EQUATIONS IN MULTICOMPONENT LIQUID AND GAS MIXTURES

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A diffusion equation is obtained for multicomponent dense gases and liquids. Approximate methods for description of mass transfer in multicomponent mixtures are analyzed.

Mass transfer in chemical technology processes occurs under such complex conditions that it becomes impossible not only to solve the problem of mass transfer even in binary mixtures, but also to formulate the problem precisely, because of the uncertainty of the boundary conditions. Thus experimental methods are utilized, employing the equation

$$N = \beta^y (y_f - y) = \beta^x (x - x_f). \tag{1}$$

Use of Eq. (1) is also justified by the fact that simultaneously with development of computation technology the complexity of mass-transfer problems has increased, so that the problem of machine time expenditure is always relevant.

In the case of multicomponent mixtures (MCM) the dimensionality of the problem increases and it is practically impossible to maintain the multiformity of MCM in experiment. The single solution presently available is to employ results obtained for binary mixtures in MCM. But basic difficulties then arise, connected with the fact that the system of mathematical-physics equations describing the mass-transfer process in MCM differs from the corresponding system for binary mixtures. The motion equation differs only in a more complex dependence of the viscosity coefficient on mixture composition, while the pressure tensor for MCM is no different than that of a pure gas [1]. The convective diffusion equations for MCM and binary mixtures do not coincide. Toor [2] and Stewart and Prober [3] have developed a method for transforming the MCM diffusion equation to binary form. This allows use of an identical system of mass-transfer equations for MCM and binary mixtures.

Two assumptions made in [2, 3] should be noted: First, it is assumed that the diffusion coefficients in the generalized Fick's law remain constant upon change in concentration from the flow core to the phase boundary; second, it is assumed that the effective interphase surface in division of MCM is equal to the surface in division of a binary mixture possessing the same physicochemical properties at the same phase expenditures.

These same assumptions are also used, strictly speaking, in employing Eq. (1) for binary mixtures of dense gases and liquids, since in the latter the diffusion coefficient as a rule is strongly dependent on composition.

Because of the complexity and incomplete nature of the theory of mixtures of dense gases and liquids, experimental material is used to describe the dependence of diffusion coefficients on composition, for example, the rule of additivity [4, 5]. In a number of studies of diffusion in binary liquids a linear dependence of the complex $\mathcal{D}_{12}[(d \ln a_1)/(d \ln x_1)]$ composition was noted [4, 6].

Most probably, this is an accidental coincidence. The complex $\mathcal{D}_{12}[(d \ln a_1)/(d \ln x_1)$ arises in consideration of the thermodynamic equations for irreversible processes. In fact, it follows from the relationships for generation of entropy that

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$$N_1 = -L_{11}\left(\frac{1}{m_1}\cdot\frac{d\mu_1}{dr_a} - \frac{1}{m_2}\cdot\frac{d\mu_2}{dr_a}\right). \tag{2}$$

Using the Gibbs–Duhem equation and the relationship $d\mu_1/dr_\alpha = RT[(d\ln a_1)/dr_\alpha]$, Eq. (2) may be transformed to the form

$$N_1 = -\mathcal{D}_{12}\left(\frac{d\ln a_1}{d\ln x_1}\right)\frac{dx_1}{dr_a}. \tag{3}$$

From this it is completely impossible to make any conclusions as to the concentration dependence of $\mathcal{D}_{12}$, since the thermodynamics of irreversible processes, like the theory of time-correlative functions [7], gives only symmetry relationships.

The concentration dependence of the diffusion coefficients in gases and liquids may be obtained by using the kinetic equation of Enskog [6]:

$$\frac{\partial f_i}{\partial t} + C_a\frac{\partial f_i}{\partial r_a} + b_{ai}\frac{\partial f_i}{\partial C_a} = \sum_p \iiint\left[\varphi\left(\mathbf{r} + \frac{\sigma}{2}\mathbf{k}_{ip}\right)\times\right.$$

$$\left.\times f_i(\mathbf{r},\ \mathbf{c}')\cdot f_p(\mathbf{r} + \sigma\mathbf{k}_{ip},\ \mathbf{c}_1') - \varphi\left(\mathbf{r} - \frac{\sigma}{2}\mathbf{k}_{ip}\right) f_i(\mathbf{r},\ \mathbf{c})\cdot f_p(\mathbf{r} - \sigma\mathbf{k}_{ip},\ \mathbf{c}_1)\right]\sigma_{ip} g d\mathbf{e}'\, d\mathbf{c}_1. \tag{4}$$

Equation (4) for isobaric isothermal diffusion can be solved by using Enskog's idea of expansion of the functions of σk_{ip} in a Taylor series and expansion of f_i in a series near the Maxwell velocity distribution. As a result the system of integrodifferential equations (4) reduces to a system of integral equations:

$$\begin{gathered}
-C_a\sum_p F_p\left[\chi x_p + \delta_{ip}\left(1 - \frac{\delta_{il}}{x_p}\right) - \chi\delta_{pl}\right] = \frac{\varphi}{n}\sum_p I_{ip}(\text{Д}^{(l)});\ i,\ l = 1,\ 2,\ 3,\ \ldots,\\
\chi = \frac{4}{3}\pi n\sigma^3\varphi,\ \delta_i(\text{Д}) = \text{Д}(\mathbf{c}) - \text{Д}(\mathbf{c}'),\\
I_{ip}(\text{Д}^{(l)}) = \iint F_i F_p[\delta_i(\text{Д}_i^{(l)} C_a) + \delta_p(\text{Д}_p^{(l)} C_a)]\,\sigma_{ip} g d\mathbf{e}' d\mathbf{c}_1.
\end{gathered} \tag{5}$$

Since the right side of Eq. (5) coincides with the right side of the corresponding expression for solution of the Boltzmann kinetic equation [1], by using an analogous expansion of the unknown Д_i in Sonin polynomials, performing orthonormalization, and then considering successively binary and multicomponent mixtures, we obtain

$$\mathcal{D}_{ip}\varphi_{ip} = \frac{3}{4}\cdot\frac{1}{n u_{ip,\,00}}, \tag{6}$$

$$-\frac{dx_i}{dr_a} = \frac{\varphi}{n}\sum_p \frac{N_i x_p - N_p x_i}{\varphi_{ip}\mathcal{D}_{ip}}. \tag{7}$$

Here $u_{ip,00}$ are irreducible integrals coinciding with the corresponding integrals for a gas with average pressure [1, 6]; $\mathcal{D}_{ip}$ and φ_{ip} are diffusion coefficients and collision-frequency increase coefficients for binary mixtures consisting of components i and p.

Since the integrals $u_{ip,00}$ are independent of concentration [1, 6], it follows from Eq. (6) that

$$\mathcal{D}_{ip}\varphi_{ip} = \mathcal{D}_{ip}^0\varphi_p = \mathcal{D}_{pi}^0\varphi_i. \tag{8}$$

TABLE 1. Diffusion Coefficients in Binary Liquid Mixtures, $\mathcal{D}_{ij} \cdot 10^5$ cm^2/sec

Experiment	By Eq. (13)	By Eq. (21)
Methanol–n-propanol		
0,819	0,825	0,826
0,856	0,850	0,856
1,049	0,945	0,951
1,063	1,040	1,049
1,128	1,141	1,155
1,266	1,251	1,262
1,707	1,611	1,625
1,863	1,895	1,895
Isobutanol–n-propanol		
0,574	0,574	
0,547	0,551	0,551
0,545	0,532	0,532
0,493	0,493	0,493
0,477	0,475	0,476
0,456	0,459	0,459
0,407	0,407	0,407
Methanol–isobutanol		
0,664	0,697	0,603
1,087	0,983	0,952
1,350	1,390	1,350
1,726	1,840	1,820

TABLE 2. Diffusion Coefficients of Toluol–Chlorobenzol–Bromobenzol Mixture, D × 10^5 cm^2/sec

D_{11}		D_{22}		D_{12}	
experimental	calculated	experimental	calculated	experimental	calculated
1,85±0,07	1,75	1,80±0,08	1,72	−0,06±0,11	−0,02
1,57±0,09	1,58	1,61±0,11	1,56	−0,08±0,10	−0,02
2,13±0,10	2,01	2,06±0,11	2,06	0,05±0,16	−0,06
1,85±0,11	1,78	1,84±0,11	1,76	0,05±0,16	−0,01
2,01±0,11	1,88	1,89±0,11	1,82	−0,02±0,03	−0,03
1,77±0,11	1,82	1,52±0,11	1,59	−0,04±0,03	−0,01

TABLE 3. Diffusion Coefficients of Methanol–n–Propanol–Isobutanol Mixture, D × 10^5 cm^2/sec [using Eq. (12)]

D_{11}		D_{33}		D_{13}	
experimental	calculated	experimental	calculated	experimental	calculated
1,04	1,01	0,88	0,81	0,03±0,02	0,01
0,91	0,90	0,72	0,70	0,03±0,04	−0,01
0,76	0,77	0,62	0,59	0,03±0,03	0,00
1,50	1,50	1,38	1,44	0,21±0,14	−0,06

TABLE 4. Comparison of Coefficients $\mathcal{D}'_{ij}$, as Determined from Eqs. (12) and (20) for Thrre-Component Ethanol Mixture

By Eq. (12)			By Eq. (20)		
$\mathcal{D}'_{12}$	$\mathcal{D}'_{13}$	$\mathcal{D}'_{23}$	$\mathcal{D}'_{12}$	$\mathcal{D}'_{13}$	$\mathcal{D}'_{23}$
0,975	1,020	0,694	0,960	1,000	0,693
0,900	0,935	0,647	0,900	0,935	0,648
0,758	0,790	0,530	0,738	0,772	0,527
1,480	1,550	1,970	1,470	1,530	1,070

Substituting Eq. (8) in Eq. (7) it is simple to obtain

$$-\frac{dx_i}{dr_a}=\frac{1}{n}\sum_p \frac{N_i x_p - N_p x_i}{\mathcal{D}'_{ip}}, \tag{9}$$

where

$$\mathcal{D}'_{ip}=\frac{\varphi_p}{\varphi}\mathcal{D}^0_{ip}=\frac{\varphi_i}{\varphi}\mathcal{D}^0_{pi}. \tag{10}$$

It is evident from Eq. (10) that the coefficients of multicomponent diffusion possess symmetry properties: $\mathcal{D}'_{ip} = \mathcal{D}'_{pi}$, and the ratio of collision-frequency coefficients of diffuse solutions are inversely proportional to the ratio of the diffusion coefficients of these solutions.

The values of the multicomponent diffusion coefficients may now be expressed in terms of the diffusion coefficients of dilute solutions and compositions of the multicomponent mixture, if it is considered that according to Hirschfelder's recommendations in the first approximation the coefficient of molecular collision-frequency increase for a mixture is defined by

$$\varphi=\sum_k x_k\varphi_k. \tag{11}$$

Substituting Eq. (11) in Eq. (10), we have

$$\mathcal{D}'_{ip}=\frac{1}{\sum\limits_k \frac{\mathcal{D}^0_{ki}}{\mathcal{D}^0_{ik}\mathcal{D}^0_{pi}}x_k}=\frac{1}{\frac{x_i}{\mathcal{D}^0_{pi}}+\frac{x_p}{\mathcal{D}^0_{ip}}+\sum\limits_{k\neq i,\,p} x_k\frac{\mathcal{D}^0_{ki}}{\mathcal{D}^0_{ik}\mathcal{D}^0_{pi}}}. \tag{12}$$

For a binary mixture, in particular, it follows from Eq. (12) that

$$\mathcal{D}_{12}=\frac{1}{\frac{1}{\mathcal{D}^0_{12}}+x_1\left(\frac{1}{\mathcal{D}^0_{21}}-\frac{1}{\mathcal{D}^0_{12}}\right)}. \tag{13}$$

Equations (12) and (13) were verified by the experimental data of [4, 5]. A comparison of $\mathcal{D}^c$ calculated with Eq. (13) and experimental $\mathcal{D}^e$ coefficients is presented in Table 1.

In Tables 2 and 3 diffusion coefficients D_{ij} obtained from Eqs. (9) and (12) are compared with experimental data on diffusion in three-component mixtures, for example:

$$N_1=-D_{11}\frac{dx_1}{dr}+D_{13}\frac{dx_3}{dr}, \tag{14}$$

$$D_{11}=\frac{\mathcal{D}'_{12}[x_1\mathcal{D}'_{23}+(1-x_1)\mathcal{D}'_{13}]}{x_1\mathcal{D}'_{23}+x_2\mathcal{D}'_{13}+x_3\mathcal{D}'_{12}}, \tag{15}$$

$$D_{13}=\frac{x_1\mathcal{D}'_{23}(\mathcal{D}'_{12}-\mathcal{D}'_{13})}{x_1\mathcal{D}'_{23}-x_2\mathcal{D}'_{13}+x_3\mathcal{D}'_{12}}. \tag{16}$$

For the toluol–chlorobenzol–bromobenzol mixture the maximum deviation from experiment does not exceed 6%, while for the alcohol mixture it comprises 3% for D_{11} and 8% for D_{33}.

Thus, in the first approximation the diffusion coefficients in a multicomponent mixture can be calculated on the basis of data on diffusion in dilute solutions. These coefficients, as follows from Tables 2 and 3, change significantly with mixture composition. Thus it follows from the first assumption made by Toor [2] and Stewart and Prober [3] that their methods are approximate. They are more accurate,

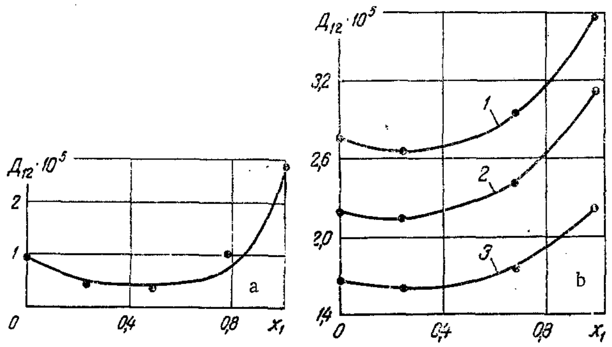

Fig. 1. Comparison of experimental and calculated diffusion coefficients (cm^2/sec) for mixtures methylcyclohexane–aniline (a) and toluol–methylcyclohexane (b). For a) $P_{12}/\varphi_1 = 8.07$; for b) $P_{12}/\varphi_1 = 1.52$; 1) 60 ± 0.01; 2) 45 ± 0.01; 3) 25 ± 0.01 °C.

the lower the motive forces of the process, i.e., the lower the difference in concentration in the flow core and at the boundary.

The diffusion equations obtained in this case permit calculation of diffusion coefficient matrices and realization of the methods of [2, 3] for both gas and liquid phases.

One must only keep in mind that Eqs. (11) and (12) do not describe cases where the dependence of diffusion coefficients on composition has a minimum, as, for example, in such nonideal liquid mixtures as methylcyclohexane–aniline, or toluol–methylcyclohexane [8]. For such mixtures we use the more accurate dependence of φ on composition [9]:

$$\varphi = 1 + a\sum_i \sum_j x_i x_j b_{ij} + \dots . \tag{17}$$

Replacing unity in Eq. (17) by $\sum_i x_i$, we obtain

$$\varphi = \sum_i x_i \left(1 + a\sum_j x_j b_{ij}\right). \tag{18}$$

One additional such change gives

$$\varphi = \sum_i x_i^2 \, \varphi_i + 2\sum_{i\neq j} \sum_{j\neq i} x_i x_j P_{ij}, \tag{19}$$

where $\varphi_i = 1 + ab_{ii}$ and P_{ij} denote the quantities $(1 + ab_{ij})$.

From Eqs. (8)-(10) we can obtain a formula more accurate than Eq. (12) for description of $\mathcal{D}'_{ij}$:

$$\frac{1}{\mathcal{D}'_{ij}} = \frac{x_i^2}{\mathcal{D}^0_{ji}} + \frac{x_j^2}{\mathcal{D}^0_{ij}} + \sum_{k\neq i,\,j} \frac{x_k^2 \mathcal{D}^0_{ki}}{\mathcal{D}^0_{ik} \mathcal{D}^0_{ji}} + 2\sum_{l\neq m} \sum_{m\neq l} \frac{x_l x_m \mathcal{D}^0_{li}}{\mathcal{D}^0_{il} \mathcal{D}^0_{ji}} \cdot \frac{P_{lm}}{\varphi_l}. \tag{20}$$

Numerical values of the ratios P_{lm}/φ_l can be found from data on diffusion in binary mixtures:

$$\mathcal{D}_{12} = \frac{1}{\dfrac{x_1^2}{\mathcal{D}^0_{21}} + \dfrac{x_2^2}{\mathcal{D}^0_{12}} + 2\,\dfrac{x_1 x_2}{\mathcal{D}^0_{21}}\,\dfrac{P_{12}}{\varphi_1}}. \tag{21}$$

Equation (21) agrees satisfactorily with the experimental data of [4, 5, 8] (Table 1, Fig. 1). In good agreement with experiment it indicates the presence of a minimum in the curve with the coordinates diffusion coefficient–concentration.

For alcohol mixtures the results obtained with Eqs. (20) and (12) practically coincide.

No less important is the problem of proper consideration of the effective interphase surface upon transition to multicomponent mixtures. It must be considered that on various portions of the interphase boundary in a stable bubble layer, for example, the effectiveness of the mass-transfer process will vary, because of hydrodynamic and geometric specifics (bubbles, jets, droplets, curvature, stability, etc.). It is thus natural to introduce the following concepts making use of distribution functions. At a point **r** to **r** + **dr** there is contained an interphase surface $\alpha(\mathbf{r})\mathbf{dr}$, characterized by a mass liberation coefficient $\beta(\mathbf{r})$. The quantity of matter transferred is then defined as

$$G=\int\limits_V [y_f(\mathrm{r})-y(\mathrm{r})]\cdot\beta(\mathrm{r})\,a(r)\,d\mathrm{r}. \tag{22}$$

For a multicomponent mixture

$$G_i=\int\limits_V \sum_{j\neq i} B_{ij}(\mathrm{r})\,[y_j(\mathrm{r})-y_{jf}(\mathrm{r})]\,a(\mathrm{r})\,d\mathrm{r}. \tag{23}$$

At the point **r** to **r** + **dr** the values of $B_{ij}(\mathbf{r})$ may be found by Toor's method [2].

However, at the present time data on $\alpha(\mathbf{r})$ and $\beta(\mathbf{r})$ are absent, and we usually take

$$G=\bar{\beta}\int (y_f-y)\,dF, \tag{24}$$

$$\frac{dG}{dF}=\bar{\beta}\,(y_f-y), \tag{25}$$

$$\frac{dG_i}{dF}=\sum_{j\neq i} B_{ij}\,(y_j-y_{jj}). \tag{26}$$

Considering Eqs. (22), (23), (25), and (26) it is easy to see that they are approximate and become exact only when the distribution functions $\alpha(\mathbf{r})$ and $\beta(\mathbf{r})$ are independent of **r**.

NOTATION

N, mass flow; F, Maxwell distribution function; Д, molecular velocity-dependent coefficients; $\mathcal{D}$, diffusion coefficient; I, integral operator; a, activity; x, y, molar fractions in liquid and gas phases; f, distribution function; r, coordinate; c, molecular velocity; C, velocity in gas-related coordinate system; **k**, unit vector in direction of centers of colliding molecules; **e**, unit vector in direction of relative velocities of colliding molecules; n, number of molecules per unit volume; φ, collision-frequency increase coefficient; B, β, mass liberation coefficient; σ, molecular diameter; σ_{ij}, differential scattering section; δ_{ij}, Kronecker delta. Indices: i, j, p, l, k, mixture components; f, interphase surface; α, vector; 0, dilute solution.

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