

# Nonequimolar Mass Transfer in Gas (Vapor)–Liquid Systems

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**Abstract**—The integral equation of a diffusion boundary layer has been analyzed to show that the existence of a resulting mass flow through the phase interface (process nonequimolarity) in two-phase gas (vapor)–liquid systems leads to the structural transformation of the traditional (phenomenological) mass-transfer equation. The application of a new structure valid for both binary and multicomponent mixtures considerably simplifies the approach to the description and generalization of any processes of mass transfer. The structure has been verified by generalizing numerous experimental data on the evaporation and condensation of pure components in an inert medium as the most typical nonequimolar processes.

**Keywords:** multicomponent diffusion, mass transfer, mass transport, two-phase system, diffusive and convective flows, mathematical description, distillation, evaporation, and condensation processes

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## INTRODUCTION

The description of mass transfer in gas (vapor)–liquid systems is almost always based on diffusion equations, and the transition from diffusion equations to mass-transfer equations is realized with any of the mass transfer theories [1, 2] and, as a rule, based on the phenomenological relationships

$$N_i = \beta_i \Delta y_i. \quad (1)$$

This approach is more or less valid for binary systems, but the mechanism of mass transfer in multicomponent mixtures becomes much more complicated. Thus, the presence (or absence) of the eigen gradient of concentrations for a considered component in the case of multicomponent diffusion yields a nowhere near complete characterization of the mechanism of its transfer, which appears as specific phenomena, such as diffusion barrier and osmotic and reverse diffusion [3]. It should also be noted that convective mass transfer also has a considerable effect on the process of multicomponent diffusion [4–7]. The mechanisms of diffusive and convective mass transfer are different, but they overlap each other, and this fact is advisable to take into account immediately in the structure of multicomponent diffusion equations [8].

It should also be mentioned that the equations of mass transfer in a two-phase gas (vapor)–liquid system are always written relative to its phase interface. Separation processes, such as absorption, desorption, evaporation, and condensation, are related by definition with the resulting (convective) flow of a separated

medium from one phase into the other, i.e., with the existence of a nonzero transversal flow velocity component on the phase interface. The absence of a transversal mass flow on the phase interface (equimolar process) can only be attained to any degree during the adiabatic distillation of mixtures that consist of components with close latent phase transition heats.

It is shown in [9] that a wide variety of allied factors (interface surface tension and phase temperature gradients, phase equilibrium line curvature) affect the process of mass transfer; a structure is proposed for a binary mass-transfer equation that takes into account the effect of these factors.

Using the theory of irreversible thermodynamics, L.A. Serafimov and A.V. Timoshenko [10] have shown that, in strict formulation, the structure of multicomponent mass-transfer equations considerably differs from the phenomenological relationships (Eq. (1)) even for an equimolar process. However, the practical application of similar structures is hardly possible (at least, in engineering approximation).

A great deal of materials on the generalization of coefficients of mass transfer for different mass-exchange equipment and phase flow interaction patterns has been accumulated based on longstanding studies [2]. The analysis of these data shows that these generalizations were most frequently derived using the tools of similarity theory presented in the form of criterial equations, and ranked by the types of processes (absorption, distillation, evaporation, etc.) and mass-exchange equipment (film apparatuses, packings, and

various kinds of bubble columns). The aforementioned generalizations were performed with a binary formulation of the problem, as the experimental study of the whole variety of multicomponent mixtures is hardly possible. At the same time, some methods have also been developed for the theoretical calculation of phenomenological coefficients of mass transfer and are currently developed, e.g., using the theory of the coupled physical and mathematical modeling of processes of mass transfer under certain hydrodynamic conditions [11, 12].

For this reason, it seems that the description of multicomponent mass transfer must be based on the use of normalized (to certain conditions) binary coefficients of mass transfer, and the specifics of a certain process must be refined immediately in the structure of mass-transfer equations. The objective of this work is to substantiate a universal structure of multicomponent mass-transfer equations suitable for describing any mass-exchange processes.

### THEORETICAL SUBSTANTIATION OF THE STRUCTURE OF THE MASS-TRANSFER EQUATION

The boundary layer theory, which enables the transition from diffusion equations to mass-transfer equations, is widely used to describe multicomponent mass transfer. In this case, the resulting (convective) mass flow through the phase interface, i.e., mass transfer nonequimolarity for each phase of a heterophase gas (vapor)–liquid system may exist on the phase interface. It is obvious that, in this case, the overall mass flow must incorporate two components, i.e.,

$$N_i = N_i^D + N_i^K. \quad (2)$$

The mass-transfer equation structure, which takes into account the effect of a convective mass flow on the mechanism of mass transfer, can be substantiated by analyzing the structure of the integral diffusion boundary layer equation derived in turn from the convective diffusion equation

$$\omega_z \frac{\partial y}{\partial z} + \omega_r \frac{\partial y}{\partial r} = \frac{\partial}{\partial r} \left[ (D + \varepsilon_D) \frac{\partial y}{\partial r} \right], \quad (3)$$

and complemented with the continuity equation

$$\frac{\partial \omega_z}{\partial z} + \frac{\partial \omega_r}{\partial r} = 0 \quad (4)$$

and the boundary conditions written for the phase interface

$$\begin{aligned} r = 0, \quad y = y_f, \quad \omega_r = N_c, \\ r = \infty, \quad y = y_\infty, \quad \frac{\partial \omega_r}{\partial r} = 0. \end{aligned} \quad (5)$$

Equation (3) is written for the most general case (liquid flow around an infinite width plate) using one

of the basic approximations of the boundary layer theory  $\left( \frac{\partial^2 y}{\partial r^2} \gg \frac{\partial^2 y}{\partial z^2} \right)$  and some additional conditions, i.e., that the liquid density in the layer is constant and the separated mixture is binary (component index is omitted). The gradient mass flow (the right part of Eq. (3)) is known to depend not only on the gradient of concentrations, but also on the gradient of temperatures and pressures in the boundary layer. The latter components can also be neglected without a great loss of precision. Thus, the numerical estimation of the thermodiffusion flow contribution into the overall diffusion flow [5, 6] shows that it does not exceed 6% of the overall mass flow, even at extremely appreciable temperature drops in the boundary layer (80–100°C).

Then, from Eq. (4), we have

$$\omega_r = N_c - \int_0^r \frac{\partial \omega_z}{\partial z} dr. \quad (6)$$

Substituting Eq. (6) into Eq. (3) and integrating the resulting expression over the entire depth of the diffusion boundary layer, we obtain the integral diffusion boundary layer equation. According to the boundary layer concept, the derivatives incorporated into Eq. (3) are zero outside the layer by definition. For this reason, the upper integration limit can be accepted as equal to both the diffusion boundary layer thickness and any values lying outside the diffusion layer (e.g.,  $\infty$ ).

Then,

$$\begin{aligned} \int_0^\infty \left[ \omega_z \frac{\partial y}{\partial z} + \left( N_c - \int_0^r \frac{\partial \omega_z}{\partial z} dr \right) \frac{\partial y}{\partial r} \right] dr \\ = (D + \varepsilon_D) \frac{\partial y}{\partial r} \Big|_0^\infty = -N^D \Big|_0^\infty = N_f^D. \end{aligned} \quad (7)$$

The integration procedure for the left part of Eq. (7) is detailed in [13]. Using this technique, we obtain

$$N_f^D = -\frac{d}{dz} \int_0^\infty \omega_z (y_\infty - y) dr - N_c (y_f - y_\infty). \quad (8)$$

The overall flow of a transferred component must also take into account convective mass transfer (Eq. (2)), i.e.,

$$\begin{aligned} N_f = N_f^D + N_f^K \\ = -\frac{d}{dz} \int_0^\infty \omega_z (y_\infty - y) dr - N_c (y_f - y_\infty) + N_c y_f. \end{aligned} \quad (9)$$

The components incorporated into the integral term of Eq. (9) depend only on the longitudinal coordinate  $z$ . The functions  $\omega_z(r)$  and  $y(r)$  are rather well studied for many practically important cases, which allows for the direct application of this equation for calculating the processes of mass transfer. When the

phenomenological approach is used, this equation discloses the physical meaning of the coefficients of mass transfer (mass transport) and can be applied for estimating the corresponding coefficients.

The relationships similar to Eq. (9) were first derived for a thermal boundary layer (G.N. Kruzhilin) and a hydrodynamic boundary layer (T. Kármán). However, they did not take into account the possible existence of a nonzero transversal velocity component on the outer flow border ( $N_c = 0$ ). The introduction of the additional nonequimolarity condition into Eq. (5) results in the appearance of the additional term  $N_c(y_f - y_\infty)$  absent in the solutions of G.N. Kruzhilin and T. Kármán in the integral diffusion boundary layer equation (Eq. (9)). This circumstance must be taken into account as early as in the substantiation of the structure of phenomenological mass-transfer equations, as in many cases the existence of a nonzero transversal velocity component on the outer border of boundary layers can have a rather profound effect on the distribution of the functions  $\omega_z(r)$  and  $y(r)$ .

When Eq. (1) is used, the physical meaning implied by the term *coefficient of mass transfer* follows from a comparison of integral diffusion using boundary layer equation (9) with phenomenological equation (9). For an equimolar process ( $N_c = 0$ ), we obtain

$$\beta^* = - \frac{\frac{d}{dz} \int_0^\infty \omega_z^* (y_\infty - y) dr}{\Delta y}. \quad (10)$$

As can be seen, Eq. (10), which is widely used in practice to describe nonequimolar processes (absorption, desorption, evaporation, condensation, etc.), does not allow one to apply this interpretation of the coefficient of mass transfer due to the transformation of the integral equation structure. In this case, the structure of the nonequimolar mass-transfer equation can be obtained by reducing an arbitrary process to reference conditions, for which it is reasonable to accept an equimolar process, i.e.,

$$N_f = \frac{\frac{d}{dz} \int_0^\infty \omega_z (y_\infty - y) dr}{\frac{d}{dz} \int_0^\infty \omega_z^* (y_\infty - y) dr} \times \beta^* \Delta y - N_c (y_f - y_\infty) + N_c y_f. \quad (11)$$

The ratio of the integral terms in the right part of Eq. (11) takes into account the transformation of the velocity and concentration profiles in the hydrodynamic and diffusion boundary layers under the action of the resulting transversal flow. The analysis showed that this ratio depends on the nature of a separated

mixture, as well as on the ratio between the longitudinal and transversal flows, i.e.,

$$\frac{\frac{d}{dz} \int_0^\infty \omega_z (y_\infty - y) dr}{\frac{d}{dz} \int_0^\infty \omega_z^* (y_\infty - y) dr} = \varphi \left( Sc, \frac{Re_c}{Re_z} \right). \quad (12)$$

At the same time, it should be noted that the velocity and concentration profiles in boundary layers are rather conservative with respect to the action of the transversal flow [13]. For this reason, it seems quite possible to neglect the correction function (Eq. (12)) in engineering calculations and set it equal to 1.

The expression  $\Delta y$  is generally used as a characteristic process driving force  $\Delta \bar{y} = y_f - \bar{y}$  in Eq. (11). This is explained by that a researcher cannot operate with the actual difference of concentrations on the diffusion layer borders ( $\Delta y = y_f - y_\infty$ ) in the most practically important cases (e.g., in the generalization of experimental data using the similarity theory tools). It is fair to say that almost all of the generalizing mass-transfer equations [2, 14] were derived using rate-average concentrations. At the same time, the second term in the right part of the integral diffusion boundary layer equation (Eq. (11)) incorporates a quite certain driving force ( $\Delta y = y_f - y_\infty$ ). Taking into account that the considered driving forces are related to one another, i.e.,

$$\bar{y} = \frac{\int_0^\infty \omega_z y dr}{\int_0^\infty \omega_z dr} \quad (13)$$

$$\text{and } p = \frac{y_f - y_\infty}{y_f - \bar{y}}. \quad (14)$$

Eq. (11) can be finally rewritten as

$$N_f = \varphi \left( Sc, \frac{Re_c}{Re} \right) \beta^* (y_f - \bar{y}) - p N_c (y_f - \bar{y}) + N_c y_f. \quad (15)$$

It is noteworthy that the integral diffusion boundary layer equation can also be obtained by other techniques; for example, it follows immediately from the balance relationships for a steady-state boundary layer. For this reason, we may state that the structure of the nonequimolar mass-transfer equation (Eq. (15)) for a binary mixture does not depend on the conditions of flow past the phase interface in principle and must be universal. The analysis of ultimate variants for the formation of concentration profiles in the diffusion boundary layer shows that the parameter  $p$  always lies

within the range  $1 \leq p \leq 2$  and may be set equal to 1.5 in the most practically important cases.

As can be seen from Eq. (15), the effect of the convective flow on the total mass flow proves to be rather complicated: the resulting mass flow linearly transforms the diffusion component of the total flow depending on its direction, and the contribution of the convective component depends on both the value and direction of the resulting flow and the boundary concentration of transferred components. The specifics of a certain process are determined by its conditions. Thus, nonequimolarity can be produced by the difference either between interface permeability conditions for diverse mixture components (absorption, desorption, etc.) or between interphase interaction heats (evaporation, condensation, etc.). It seems that the generalizing equations derived to describe different processes of mass transfer must come to a universal equation normalized with respect to equimolar process conditions when the proposed mass-transfer equation structure is used, as the nonequimolarity effects have already been taken into account in the structure of Eq. (15).

When passing to multicomponent mixtures, the multicomponent convective diffusion equation takes the form

$$\omega_z \left( \frac{\partial y}{\partial z} \right) + \omega_r \left( \frac{\partial y}{\partial r} \right) = \frac{\partial}{\partial r} \left\{ [\bar{D}] \left( \frac{\partial y}{\partial r} \right) + \varepsilon_D \left( \frac{\partial y}{\partial r} \right) \right\}. \quad (16)$$

The direct application of this equation does not allow one to obtain the structure of the multicomponent mass-transfer equation. However, a corresponding solution can be found by linearizing Eq. (16), the procedure for which is described in sufficient detail in [3, 15]. The problem does not radically change upon the transition to convective diffusion equations. Linearizing the diffusion equation (Eq. (16)) using a diagonalizing matrix and introducing the additional assumption about the constancy of elements in the square matrix of multicomponent diffusion coefficients, we then obtain

$$\begin{aligned} & \omega_z \left( \frac{\partial \Psi}{\partial z} \right) + \omega_r \left( \frac{\partial \Psi}{\partial r} \right) \\ &= \frac{\partial}{\partial r} \left\{ \langle D_L \rangle \left( \frac{\partial \Psi}{\partial r} \right) + \varepsilon_D \left( \frac{\partial \Psi}{\partial r} \right) \right\} = \frac{\partial}{\partial r} \left\{ \langle D_L + \varepsilon_D \rangle \left( \frac{\partial \Psi}{\partial r} \right) \right\}. \end{aligned} \quad (17)$$

As can be seen, the linearization splits the set of multicomponent convective diffusion equations (16) into a number of linear differential equations, in which the concentrations  $y$  are replaced by their linear combinations  $\Psi$  (pseudoconcentrations), and the diagonal matrix elements  $D_L$  are used instead of binary diffusion coefficients. The form of the obtained differential equations is entirely the same as for the convective diffusion equation for binary mixtures (Eq. (3)), which enables one to use the above-found solution

(Eq. (15)). Neglecting the correction function (Eq. (12)), this equation can be written as

$$(\eta_f) = \langle B_L \rangle (\psi_f - \bar{\psi}) - p N_c (\psi_f - \bar{\psi}) + N_c (\psi_f). \quad (18)$$

Performing inverse transformations, for a multicomponent mixture, we finally obtain that

$$(N_f) = [B^*] (y_f - \bar{y}) - p N_c (y_f - \bar{y}) + N_c (y_f). \quad (19)$$

The elements of the multicomponent equimolar-mass-transfer matrix can be calculated by different methods [15]. Here, it should be noted that the method selected to express the multicomponent mass transfer matrix elements must meet the Damkeler

condition  $\left( \sum_{i=1}^m N_i^* = 0 \right)$ . In this context, it seems preferable to use the equation [16] proposed specially for describing multicomponent equimolar mass transfer, namely,

$$N_i^* = \sum_{j \neq i}^m \beta_{ij}^* (y_{ij} \bar{y}_j - y_{ji} \bar{y}_i) = [B^*] (y_f - \bar{y}), \quad (20)$$

$$\text{where } B_{ii}^* = \sum_{j \neq i}^m \beta_{ij}^* y_j \quad (21)$$

$$\text{and } B_{ij}^* = -\beta_{ij}^* y_i. \quad (22)$$

Hence, set of equations (19)–(22) principally describes the gas-phase mass transfer in multicomponent mixtures for any mass-exchange process in gas(vapor)–liquid systems if the information about the regularities of resulting flow distribution along the phase interface is available, and the binary coefficients of mass transfer, which corresponds to conditions of the equimolar process, is the only type of kinetic coefficient used. In this case, the direction of mass flow from the outer flow border (phase interface) to the flow core is taken as positive. The commonly accepted phenomenological equation (Eq. (1)) is a particular case of this system for a binary mixture.

#### EXPERIMENTAL VERIFICATION OF THE PROPOSED STRUCTURE OF THE MASS-TRANSFER EQUATION

There are many known experimental works devoted to the study of certain mass-exchange processes that are characterized by a given degree of nonequimolarity. The results of the study are traditionally formalized as special criterial equations, which generalize the information about the coefficients of mass transfer in certain processes under certain hydrodynamic conditions. Only a small number of works pretends to the generalization of a group of processes in similar apparatuses. Thus, it is communicated in work [17] that the data of a number of studies on the evaporation of water into air and the absorption of  $\text{NH}_3$  with water in film apparatuses can include processes with a

universal criterial equation. However, this method is always accompanied by a general loss of precision.

It was not as early as by von Kármán that the commonly accepted criterial equation written as the power dependences of the Sherwood criterion on influence criteria (Sh, Re, etc.) is incorrect, as the power exponents in the criterial equation must be functions of the same criteria. Equimolar mass exchange was studied in [18] using the mathematical model of turbulent mass exchange in an axially symmetric gas flow (pipe) to show that the following equation proposed by von Kármán really provides a higher generalization precision:

$$\text{Sh} = \frac{0.0345 \text{Re}^{0.75} \text{Sc}}{1 + 0.75 \text{Re}^{-0.08} \{\text{Sc} - 1 + \ln[(1 + 5\text{Sc})/6]\}}. \quad (23)$$

The criterial equations that generalize gas-phase mass transfer in film columns are compared in Fig. 1 for three typical mass-exchange processes, e.g., evaporation ( $N_c > 0$ ), distillation ( $N_c \approx 0$ ), and absorption ( $N_c < 0$ ).

As can be seen, all of the considered generalizations can be distinctly classified into three corresponding groups, i.e., the generalization lines for evaporation (lines 1–3) predominantly lie above the generalization lines for distillation (lines 4–9), and the generalization lines for absorption (lines 10 and 11) are below them, which confirms the hypothesis about the appreciable effect of the convective (resulting) flow on the process of mass transfer.

The data (points) calculated by Eq. (23) are plotted in the same figure. Since this equation was derived based on a numerical experiment, they may be considered to be theoretical. As can be seen, these data correlate well with the experimental generalization data for distillation, which supports the advisability of numerical experiments for acquiring corresponding information (generalizing equations).

The evaporation and condensation of pure components in an inert medium are the most typical representatives of nonequimolar processes. These processes are rather widely used in industry, quite well studied, and are of particular theoretical interest, for the following reasons:

(1) The resistance of the gas phase to mass transfer is eliminated during the evaporation (condensation) of one-component liquids, which enables the overall process of mass transfer to be reduced to gas-phase mass transfer.

(2) The conditions of the isothermal process eliminate the effect of heat transfer on the process of mass transfer.

(3) The insolubility of an inert component in the liquid phase enables the fairly simple estimation of the resulting mass flow as the flow of an active (evaporated or condensed) mixture component.

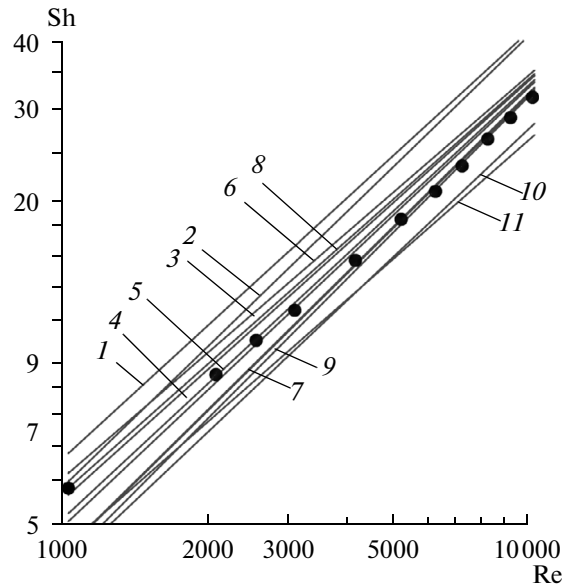


Fig. 1. Data on the gas-phase mass transfer in film columns ( $\text{Sh} = f(\text{Re})$  at  $\text{Sc} = 0.75$ ) for (1–3) evaporation, (4–9) distillation, and (10, 11) absorption from (1) [17], (5, 6) [19], (7) [20], and (2–4, 8–11) [2]. Points show data calculated by Eq. (23).

It should also be noted that the most correct information about the effect of the convective flow on resulting mass exchange can be obtained by performing the experiment on the evaporation and condensation of just pure components in an inert medium (binary formulation), since in this case the diffusion effect of interaction between different system components are eliminated (multicomponent formulation).

The undoubted effect of the concentration of an inert component on mass transfer in the process of evaporation was mentioned in a number of earlier works. It was proposed as early as in the works of Colburn and Drew [21] and Spalding [22] that the effect of a change in the concentration of an inert component in the diffusion layer be taken into account as follows:

$$\text{Sh} = \frac{1}{(1 - y)_{\text{in}}} f(\text{Re}, \text{Sc}). \quad (24)$$

Relying on the generalization of evaporation experimental data, Cairns and Roper [23] derived the following equation:

$$\text{Sh}(1 - y)_{\text{in}}^{0.83} = 0.021 \text{Re}^{0.83} \text{Sc}^{0.44}. \quad (25)$$

A number of authors also noted the effect of some other criteria and complexes, in particular the process driving force (difference between the concentrations on the diffusion layer borders) and the heterogeneity of a mixture (ratios of the molecular masses of the gas mixtures on the diffusion layer borders or their densities), on mass transfer. Thus, Asano and Fujita [24]

have processed a great deal of experimental data on the evaporation of water, benzene, carbon tetrachloride into air and the evaporation of water into carbon dioxide using the equation

$$\text{Sh}_f(1 - Y_f) = 0.41 \text{Re}^{0.67} \text{Sc}_f^{0.5} (1 + B)^{0.79} (\rho_f/\rho_\infty)^{-0.07}, \quad (26)$$

$$\text{where } B = \frac{Y_f - Y_\infty}{1 - Y_\infty}. \quad (27)$$

Asano and Fujita [24] use relative mass concentrations instead of molar concentrations in their generalizations. Similar generalizations were also obtained in the works of a number of other authors [25].

Relying on these studies and a number of other works, it has been proposed [26–28] to reduce the process of mass transfer in the evaporation or condensation of pure components in an inert medium to certain reference conditions defined as arising in the process of mass transfer under similar hydrodynamic conditions ( $\text{Re} = \text{idem}$ ,  $\text{Sc} = \text{idem}$ ), but at a vanishingly small diffusion flow rate, i.e.,

$$\frac{\text{Sh}_D}{\text{Sh}_D^I} = f\left(\text{Re}, \text{Sc}, \text{Ar}, y_\infty, \Delta y, \frac{M_f}{M_\infty}\right). \quad (28)$$

This approach was most consistently applied in the works of L.D. Berman. This author has led to the important conclusion [28] that the ratio  $\text{Sh}_D/\text{Sh}_D^I$  is weakly dependent on the pattern and conditions of flow past the phase interface, which indicates the wide applicability of these generalizations. L.D. Berman has performed the processing of numerous experimental data [23, 26–28] obtained in both his works and the works of some other authors to show that the experimental evaporation data can perfectly be generalized for different components and hydrodynamic process conditions at a negligible mixture heterogeneity factor ( $\rho_f/\rho_\infty = 1$  or  $M_f/M_\infty = 1$ ) with the relatively simple equation

$$\frac{\text{Sh}_D}{\text{Sh}_D^I} = \frac{(e - 1)}{(e - 0.4)}, \quad (29)$$

$$\text{where } e = \frac{1 - y_\infty}{y_f - y_\infty}. \quad (30)$$

L.D. Berman points out that Eq. (29) can also be extended to the generalization of the condensation process. In these equations,  $e$  is the factor, which takes into account the component evaporation rate on the phase interface and interpreted by some authors as a similarity criterion. Low values of the factor  $e$  correspond to high evaporation rates, and its high values indicate that the evaporation rate is low. In this case, the reference conditions are understood to mean the process occurring at a vanishingly small evaporation rate ( $e \rightarrow \infty$ ,  $\Delta y \rightarrow 0$ ). It should be noted that the considered approach implies that driving forces of mass transfer and coefficients are calculated using flow core component concentrations instead of mass-average

concentrations accepted when deriving the structure of Eq. (15). The dependence  $\frac{\text{Sh}}{\text{Sh}_D^I} \Delta y = f(e)$ , in which the Sherwood criterion is calculated for the total mass flow, is used in the generalizations of some authors. It can easily be shown that these expressions are entirely equivalent to Eq. (28) as follows:

$$\frac{\text{Sh}}{\text{Sh}_D^I} \Delta y = \frac{\text{Sh}_D}{\text{Sh}_D^I} (e - 1)^{-1}. \quad (31)$$

Neglecting the mixture heterogeneity factor ( $\rho_f/\rho_\infty = 1$ ), Eq. (26) can similarly be reduced to the form

$$\frac{\text{Sh}_D}{\text{Sh}_D^I} = \left(\frac{e}{e - 1}\right)^{-0.79}. \quad (32)$$

All of the analyzed generalizations are in rather good agreement with both the experiment and each other. Hence, we may state that, according to contemporary concepts, there is an explicit dependence between the mass flow of an active mixture component and both the inert component concentration and the process driving force in the evaporation (condensation) of a component in an inert medium for binary mixtures, although the opinions about a certain form of these dependences are rather contradictory. It is also noteworthy that the dependence of the coefficients of mass transfer on the transferred component concentrations and, moreover, on the driving forces of the process contradicts the essence of the phenomenological approach. These dependences can be taken into account to any extent for binary mixtures, but this is impossible for multicomponent mixtures in principle.

The most general and substantiated information about the criteria characterizing the process of mass transfer can be obtained from the analysis of differential mass-transfer equations, i.e., convective diffusion equations. To accomplish this, it is advisable to use the above-considered integral equations of a diffusion boundary layer. There is no diffusion resistance to mass transfer in the liquid phase for the isothermal evaporation (condensation) of pure components in an inert medium, the resulting mass flow through the phase interface is equal to the active mixture component flow ( $N_c = N$ ). When the correction function (Eq. (12)) is neglected, and the coefficients of mass transfer are determined from the real difference of concentrations on the diffusion layer borders, it then follows from Eq. (15) (component index is omitted) that

$$N_D = N(1 - y_f) = \beta^*(y_f - y_\infty) \frac{(1 - y_f)}{(1 - y_\infty)} \quad (33)$$

$$\text{and } \text{Sh}_D = \text{Sh}^* \frac{(1 - y_f)}{(1 - y_\infty)}. \quad (34)$$

When the same nonequimolar diffusion process is selected as a reference process but at a vanishingly

small rate ( $Sh_D^I = Sh_D|_{\Delta y \rightarrow 0}$ ), the formal transformation of Eq. (34) then gives

$$\frac{Sh_D}{Sh_D^I} = \frac{Sh_D}{Sh^*} = \frac{e-1}{e} \quad (35)$$

Since Eq. (35) was derived without any limitations on the type of the process, it is equally applicable for any mass-exchange process in gas (vapor)–liquid systems, including the considered processes of evaporation and condensation. However, we should note that the criterion  $e$  proves to be negative for the process of condensation ( $y_f - y_\infty < 0$ ). Minimum  $e$  is 1 ( $y_\infty \rightarrow 0$ ) for evaporation, and  $Sh_D/Sh_D^I \rightarrow 0$  in this case, whereas minimum  $e = -\infty$  and maximum  $e$  is zero ( $y_\infty \rightarrow 1$ ) for condensation. In the latter case, as also pointed out in [26], the ratio  $Sh_D/Sh_D^I \rightarrow \infty$ . Equation (35) perfectly meets these ultimate process conditions, but the same cannot be said of Eqs. (29)–(31).

It should also be noted that the acceptance of the condition  $Sh_D^I = Sh^*$  used in the derivation of Eq. (35) is equivalent to the assumption about the coincidence of concentration profiles for equimolar and non-equimolar processes under the conditions of their low rates. By all means, this assumption contradicts with the physical essence of the process. It immediately follows from Eq. (34) that, for evaporation,  $N_D^I < N^*$  and, for condensation, if there exists a finite driving force,  $N_D^I > N^*$ ; otherwise, it is impossible to speak of mass transfer. At the same time, the coefficients of mass transfer are determined during the selection of equivalent conditions in both approaches under the same hydrodynamic conditions as for the studied non-equimolar process ( $Re = idem$ ,  $Sc = idem$ ), and this in turn implies the equality of rate-average concentrations ( $\bar{y} = idem$ ). This circumstance allows us to establish a relation between the compared approaches.

It follows from the boundary layer theory that the thickness of the boundary layer grows for the positive direction of the resulting flow (evaporation,  $N_c > 0$ ), and the derivatives  $(\frac{\partial y}{\partial r})$  in Eq. (2) decrease [13], which leads to a decrease in diffusion coefficients of mass transfer. At a vanishingly small evaporation rate ( $\Delta y \rightarrow 0$ ), the diffusion component of the mass flow becomes much lower than its convective component ( $N_c y_f$ ). In this case, the concentrations in the diffusion layer are equalized, and a slight change in concentration occurs only in the zone adjacent to the flow core ( $y_f \rightarrow \bar{y}$ ). Then, it follows from Eq. (34) that

$$Sh_D^I = Sh^* \frac{(1-\bar{y})}{(1-y_\infty)} \quad (36)$$

Similarly, it is possible to demonstrate for the process of condensation that  $y_f \rightarrow \bar{y}$ , and

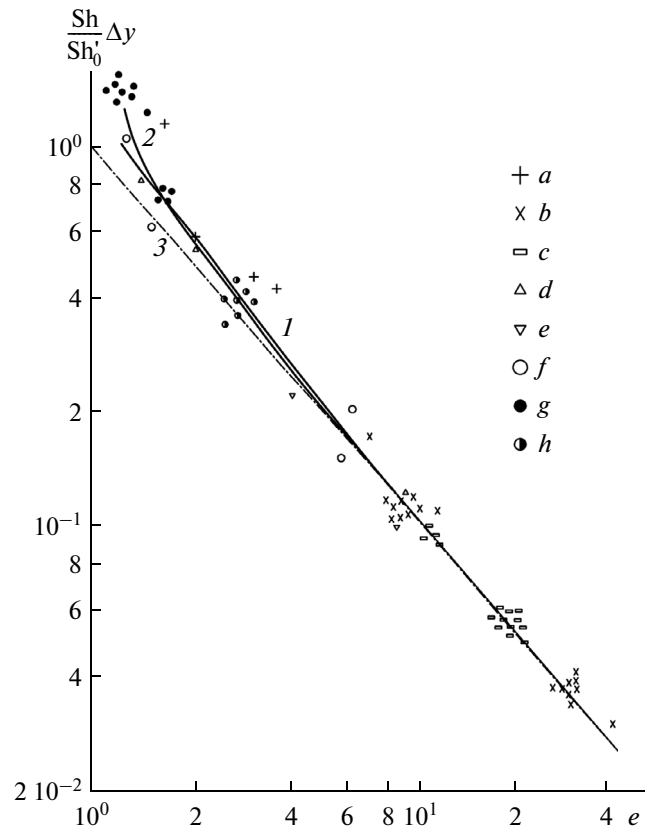


Fig. 2. Relative Schmidt criterion versus evaporation intensity factor  $e$ : (1) nearly coinciding data of calculation by Eqs. (29) and (38), (2, 3) calculation by Eqs. (32) and (35), respectively. All the equations were rearranged in the form of Eq. (31). Points are the data from [27] for (a–c) water–air, (d) chlorobenzene–air, and (e) bromobenzene–air and from [24] for (f, g) carbon tetrachloride–air, and (h) methanol–air.

$$Sh_D^I = Sh^* \frac{(1-y_f)}{(1-\bar{y})} \quad (37)$$

at  $\Delta y \rightarrow 0$ .

Then, performing the simultaneous solution of Eqs. (14), (33), and (35) at a fixed parameter  $p = 1.5$ , for the processes of evaporation and condensation, we obtain that

$$\frac{Sh_D}{Sh_D^I} = \frac{(e-1)}{(e-0.333)} \quad (38)$$

$$\text{and } \frac{Sh_D}{Sh_D^I} = \frac{(e-0.333)}{e} \quad (39)$$

A comparison of all of the considered generalizing equations with the experimental data on the evaporation of different components into an inert medium (air) from [23–28] is carried out in Fig. 2.

As can be seen, appreciable deviations between the experimental data and Eq. (35) derived immediately from the structure of the binary nonequimolar mass-transfer equation (Eq. (15)) are only observed in the

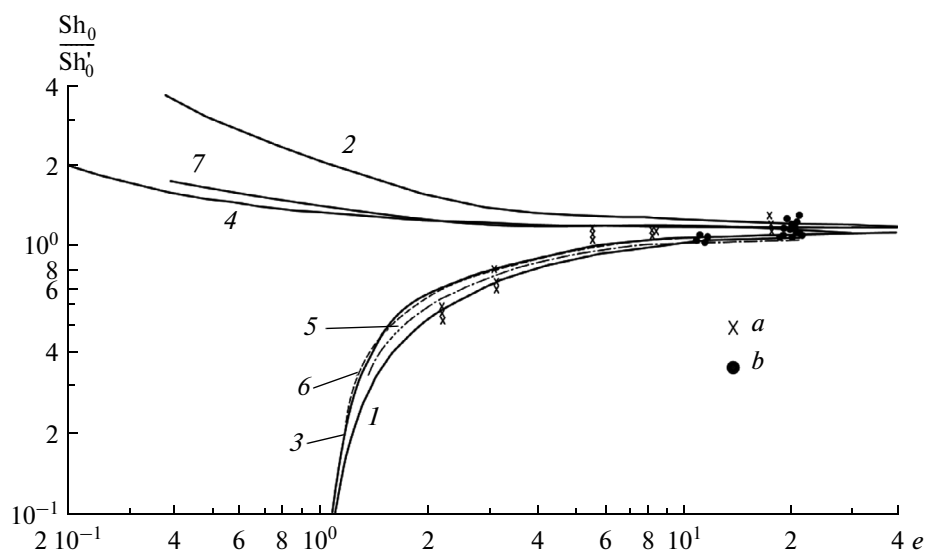


Fig. 3. Mass and heat transfer in evaporation and condensation: calculation of mass transfer in (1) evaporation and (2) condensation by Eq. (35), (3) evaporation and (4) condensation by Eq. (29), (5) evaporation by Eq. (32), (6) evaporation by Eq. (38), and (7) condensation by Eq. (39); data for heat transfer (points) in evaporation (water–air) from (a) [29] and (b) [27].

region of rather high evaporation rates ( $e < 1.5$ ). We should note that the spread of experimental data in this region is rather great, as the process isothermicity condition is hard to maintain at such a high evaporation rate.

Let us emphasize once again the following important circumstance: a researcher almost always determines the total mass flow through the phase interface from the expression ( $N_f = G_{fin}\bar{y}_{fin} - G_{ini}\bar{y}_{ini}$ ), i.e., operates with mass-average flow rates and concentrations for any apparatuses or their elements. However, both the flow rates and compositions of interacting phases are variable for nonequimolar processes. This approach also persists when calculating driving forces of the process and, therefore, in the calculation of the coefficients of mass transfer and similarity criteria. At the same time, as can be seen from Eq. (14), the difference between the compared driving forces ( $y_f - y_\infty$ ) and ( $y_f - \bar{y}$ ) may be very considerable.

A comparison of the generalizing equations with each other and the experimental data for the processes of evaporation and condensation is performed in Fig. 3. For the process of condensation, absolute evaporation intensity factors are plotted as abscissas. The data on the generalization of heat-exchange processes are plotted in the same figure. Under the assumption about the existence of perfect analogy between these processes in apparatuses of the same type, the following condition [13] must be met:

$$\frac{Sh_D}{Sh_D^I} = \frac{Nu}{Nu^I} = f(e). \quad (40)$$

As can be seen, the data on mass and heat transfer also rather satisfactorily correlate with each other,

which allows one to speak of the applicability of the assumption of the existence of a perfect analogy between separately occurring mass and heat transfer processes in apparatuses of the same type for calculating the corresponding coefficients of mass transfer in the absence of reliable information on one of the processes.

## CONCLUSIONS

The existence of a convective mass flow through the phase interface affects the structure of the integral diffusion boundary layer equation and leads to the appearance of an additional term. For this reason, the application of the traditional phenomenological structure of the mass-transfer equation (Eq. (1)) for describing mass-exchange processes with pronounced nonequimolarity seems to be unjustified. The analysis of the integral equation has allowed us to propose a corrected structure of the phenomenological equation based on reducing the arbitrary mass-exchange process to a reference process that was selected to be equimolar. The proposed mass-transfer equation structure was shown to be valid for both binary and multicomponent mixtures.

The generalization criteria (evaporation and condensation intensity factors) used in a number of works for describing extremely nonequimolar processes immediately follow from the proposed structure of the mass-transfer equation itself, thus implicitly validating its correctness. The considered generalization (similarity) criteria represent concentration dependences and are only correct in this form in the binary formulation of the problem (evaporation or condensation of



pure components in an inert medium). Moreover, in our opinion, these dependences cannot act as similarity criteria at all, as they result from the incorrectness of the used structure of the phenomenological mass-transfer equation. An important advantage of the proposed structure is its universality, i.e., its applicability to describing arbitrary mass-exchange processes.

### NOTATION

$B^*$ —elements of the square matrix of multicomponent equimolar coefficients of mass transfer, m/s;

$B_L$ —elements of the diagonal matrix of coefficients of mass transfer, m/s;

$D$ ,  $\bar{D}$ , and  $D_L$ —binary diffusion coefficients and elements of the square and diagonal matrices of multicomponent diffusion, respectively,  $m^2/s$ ;

$N$ —mass flow, m/s;

$y$ —molar gas concentration;

$\Delta y$ —driving forces of mass transfer;

$r$  and  $z$ —transversal and longitudinal coordinates, respectively;

$\beta$ —coefficient of mass transfer for a binary mixture, m/s;

$\varepsilon_D$ —turbulent diffusion coefficient,  $m^2/s$ ;

$\eta$  and  $\psi$ —pseudoflows and pseudoconcentrations of the linearized multicomponent mass-transfer equation, respectively;

$\omega$ —velocity, m/s;

[ ], ( ), and < >—square, column, and diagonal matrices, respectively;

$Nu = al/\lambda$ —Nusselt criterion;

$Re = \omega l/\nu$ —Reynolds criterion;

$Sh = \beta l/D$ —Sherwood criterion;

$Sc = \nu/D$ —Schmidt criterion.

### SUBSCRIPTS AND SUPERSSCRIPTS

$D$  and  $K$ —diffusive and convective mass flow components, respectively;

$i, j$ —components;

$f$ —phase interface;

$c$ —resulting flow;

$z, r$ —directions of coordinate axes;

$\infty$ —flow core;

\*—equimolar conditions;

—mass-average values.

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