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COMPARISON OF METHODS OF DESCRIBING MASS TRANSFER IN MULTICOMPONENT MIXTURES

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The accuracy of three basic approximate methods of describing mass transfer in multicomponent mixtures is estimated by using a mathematical model of intraphase mass transfer.

One of the main trends in the improvement of methods of calculating separation processes in multicomponent mixtures (MCM) in chemical engineering involves taking account of the kinetic equations of mass transfer. In spite of the considerable number of papers which have been published in this field, the kinetics of mass transfer has not been adequately studied. As a result of the extreme complexity of convective mass-transfer problems and the inadequate study of molecular and turbulent diffusion, all the methods of describing multicomponent mass transfer so far developed are approximate. The question of accuracy and the limits of applicability of these methods remains debatable, since physical experiments [1, 2] and their comparison with calculational methods proposed in the literature [3] so far cannot give a comprehensive answer.

The present paper is devoted to an analysis of the accuracy of various approximate methods of describing mass transfer and the development of recommendations for their use in mathematical models.

The equations describing mass transfer in multicomponent mixtures have the form [4]

$$N_i = \sum_{j=1}^{n} \mathbf{B}_{ij} (y_{jf} - y_j). \tag{1}$$

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TABLE 1. Comparison of Approximate and Accurate Methods

Method 1		Method 2		Method 3	
ΔN_1	ΔN_2	ΔN_1	ΔN_2	ΔN_1	ΔN_2
1,25	10,61	1,56	26,51	1,59	47,34
0,68	—5,49	0,18	7,85	—0,24	31,45

The main difficulty in using these relations is the lack of information on the matrix of the transfer coefficients.

The complexity and characteristics of the transfer equations in an MCM prevent the use of the apparatus of similarity theory and make it impossible to generalize the experimental data on multicomponent mass transfer.

Several approximate methods of describing mass transfer in an MCM have been proposed to satisfy the requirements of design practice. These methods are based on theoretical and experimental investigations of binary mixtures. Three main methods can be singled out.

Method 1. Linearized Mass-Transfer Theory. The basic assumptions of this theory are discussed in [4, 5]. In this method the matrix [B] is determined from the equations

$$[\mathbf{B}] = [M]\ulcorner \mathbf{B}_k \lrcorner [M]^{-1}, \tag{2}$$

$$[M]^{-1}[\mathbf{D}][M] = \ulcorner \mathbf{D}_k \lrcorner. \tag{3}$$

The pseudobinary mass-transfer coefficients $\mathbf{B}_k$ are calculated from the dimensionless equations of binary mixtures into which the pseudobinary diffusion coefficients $\mathbf{D}_k$ and the physicochemical parameters of the multicomponent mixture have been substituted.

Method 2. This method is based on the replacement of the true dependence of the matrix [B] on composition by a linear relation [6]:

$$\mathbf{B}_{ii} = \sum_{k \neq i}^{n} \beta_{ik} y_k, \quad \mathbf{B}_{ij} = -\beta_{ij} y_i. \tag{4}$$

The constants in this linear approximation are the binary mass-transfer coefficients β_{ij}.

Method 3. Independent Mass Transfer. This method is based on an average effective mass-transfer coefficient. The transfer of a component is described by the equations for binary mixtures [7, 8]:

$$\mathbf{B}_{ii} = \beta_{i\,\mathrm{eff}}, \quad \mathbf{B}_{ij} = 0 \quad (i \neq j). \tag{5}$$

With a certain degree of arbitrariness, depending on the assumptions made, it can be assumed that the linearization method is the most accurate and the method of independent determination of the flux of each component is the crudest. However, this order is not rigorously justified, and a detailed test of the accuracy of all these methods is necessary, especially since they differ considerably in the labor involved.

The accuracy and range of applicability of the approximate methods can be tested by a computation using more detailed models which take account of elementary mass, momentum, and energy-transfer events and include the equations of hydrodynamics and molecular and eddy convective diffusion.

The development of such models of interphase mass transfer, henceforth called accurate, involves considerable difficulties and so far is possible only in the simplest cases for processes occuring in devices with well-studied hydrodynamics (axisymmetric and plane boundary-layer turbulence). We chose the case of a turbulent mass flux in a straight circular pipe for analysis.

A detailed description of the mathematical model of interphase mass transfer under these conditions is given in [9, 10]. The model was realized on an M-222 computer.

The accuracy of approximate methods of describing mass transfer in an MCM was estimated by numerical experimentation with an accurate model of interphase mass transfer. This is a valid estimate since the mathematical model adequately reflects the physical process [10, 11].

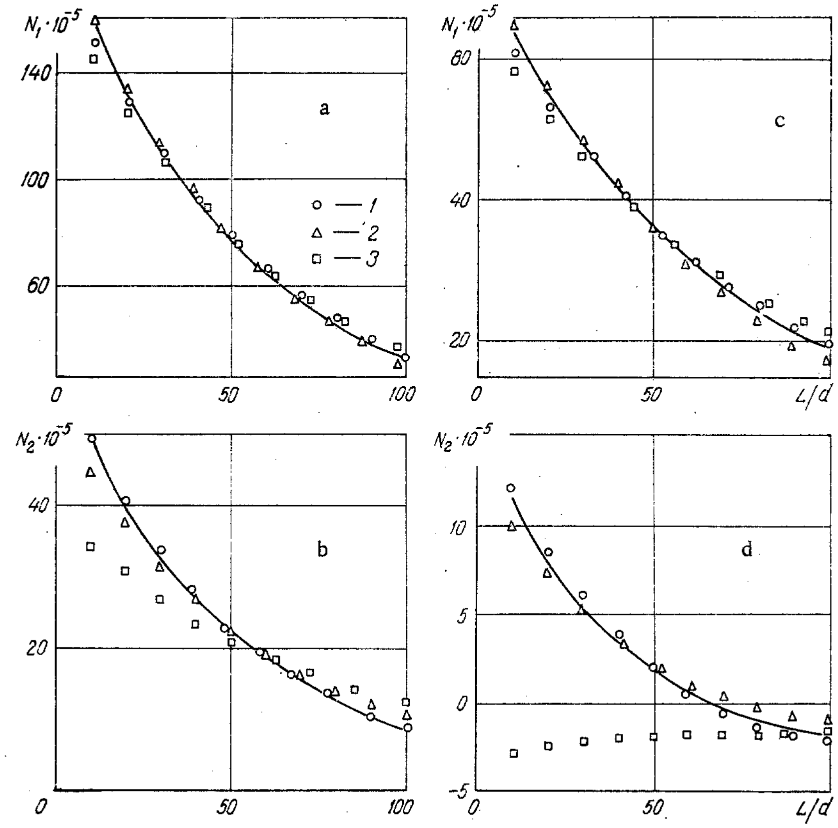

Fig. 1. Comparison of approximate and accurate solutions: a, b) mass transfer under the action of large driving forces on all components (in Fig. 1a the numbers 1-3 are the numbers of the methods); c, d) moderate driving forces.

The calculations were performed with binary and multicomponent mixtures. The governing parameters in the calculational process, Re, Sc, and L/D, were varied over the following limits:

$$10^4 \leqslant \mathrm{Re} \leqslant 10^5;\ 0.5 \leqslant \mathrm{Sc} \leqslant 8;\ 0 < L/d < 100.$$

A numerical experiment on mass transfer in binary systems was performed to obtain data on mass-transfer coefficients for subsequent use in engineering calculations.

The calculations showed that the dependence of the Sherwood number on the Reynolds and Schmidt numbers can be approximated to within 1% by the following expression:

$$\mathrm{Sh} = \frac{0.0345\,\mathrm{Re}^{0.75}\,\mathrm{Sc}}{1 + 0.75\,\mathrm{Re}^{-0.09}\left[\mathrm{Sc} - 1 + \ln\left(\frac{1+5\,\mathrm{Sc}}{6}\right)\right]}. \tag{6}$$

The experiment with an MCM was performed on three-component systems, since the difference between the approximate and accurate solutions is maximum for ternary mixtures. The concentrations of components at the entrance to the model apparatus were chosen from considerations of symmetry and uniform coverage of concentration space. The calculations were performed for mixtures with various relative fugacity coefficients and various maximum ratios of the binary diffusion coefficients. The results were compared directly by means of profiles of the variation of concentrations and fluxes of the components over the height of the apparatus.

Before proceeding to a discussion of the numerical experiment, certain features of the calculation of mass transfer by the approximate methods must be discussed. In Method 1 there is an indeterminacy in the method of calculating matrix [B] since it is not known what composition of the mixture should be used in determining it. Calculations showed that the composition of the gas entering the apparatus can be used without a significant loss of accuracy; using the composition averaged over the process improves the convergence to the accurate solution by only tenths of a percent. Method 3 requires finding the effective mass-transfer coefficients. The authors of this method propose to determine $\beta_{i\,\mathrm{eff}}$ in terms of $D_{i\,\mathrm{eff}}$ by a dimensionless equation. However, $\beta_{i\,\mathrm{eff}}$ can also be found from the binary mass-transfer coefficients

$$\beta_{i\,\mathrm{eff}} = \sum_{j \neq i} \beta_{ij} y_j/(1 - y_i). \tag{7}$$

Calculations performed over a wide range of variation of properties and mass-transfer conditions showed that the values of the $\beta_{i\,\mathrm{eff}}$ determined from Eq. (7) more accurately represent the process than do the values determined from the $D_{i\,\mathrm{eff}}$.

In estimating the accuracy of the approximate methods of describing mass transfer in an MCM it should be noted that we did not succeed in finding a definite dependence of the deviation of the approximate solutions from the accurate solution for a variation of the parameters affecting the process. Although these deviations cannot be called random, they were estimated by such mathematical statistics tests as Δ_0 and M_0.

A comparison of methods over the whole set of experiments performed (Table 1) shows that on the whole the methods do not differ in accuracy as much as might be expected from an analysis of the assumptions made. This is particularly noticeable in the description of the flux of the first component, where it is impossible to indicate a preference for one of these methods. The first method is on the whole more accurate in describing the flux of the second component, although there are experiments in which Method 2 gives a better description of the motion of all the components. The graphs in Fig. 1a-d show the typical behavior of three-component systems predicted by the different methods. Figure 1a, b represents mass transfer under the action of large driving forces on all components; Fig. 1c, d is for moderate driving forces when the characteristics of the diffusion interaction of the components have already appeared. It is clear from these graphs that the three methods are practically equivalent in the description of the behavior of the first component, while Method 3 at first glance is unsatisfactory in describing the middle component. It should be noted, however, that the fluxes of the first and second components generally differ by an order of magnitude, with the first component being transferred preferentially, and the character of the transfer of the second component results mainly from forces of the diffusion interaction, which numerical experiment showed to be small. Therefore, in a number of practical situations when a clear separation of the middle components is not required (absorption of gaseous hydrocarbons, stabilization of gasoline, catalyzers, oils etc.) and an error of even 50% in determining the flux of the middle component does not change the general picture of the transfer, the accuracy of all three methods can be considered satisfactory. Nevertheless, when strict requirements are imposed on the sharpness of the separation of the middle components, for example, in the separation of small amounts of admixtures by rectification or in the design of a process in the distillation part of an absorption-stripping column, Method 3 may not only give an appreciable quantitative error, but may even falsely predict the qualitative behavior of a multicomponent system in the mass-transfer process.

Taking this into account and also taking account of the differences in the complexity of calculations of the most general case of the kinetics of the mass-transfer process made with the different approximate methods, it is recommended that Method 2 be used in the mathematical models of column devices to solve a wide class of practical problems. The first method is the most accurate, but it should be applied only in the most important cases, since it requires a considerable expenditure of machine time, even with modern computers.

NOTATION

y, concentration of component in gas; N, mass flux; D, $\mathbf{D}$, coefficients of molecular diffusion in binary and multicomponent mixtures, respectively; β, $\mathbf{B}$, mass-transfer coefficients in binary and multicomponent mixtures, respectively; d, pipe diameter; L, pipe length; Δ_0, mean relative deviation, %; M_0, mathematical expectation of relative deviation, %; Sh, Sherwood number; Sc, Schmidt number; Re, Reynolds number; [ ], square matrix; ⌜ ⌟, diagonal matrix; i, j, k, numbers of components of the mixture; n, number of components; f, phase interface; eff, effective.

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AN EXPERIMENTAL DEVICE FOR MEASUREMENT OF THERMAL CONDUCTIVITY OF DIAMOND MONOCRYSTALS

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An experimental device and technique for measurement of thermal conductivity in diamond monocrystals are described. The temperature dependence of thermal conductivity of natural and synthetic diamonds is presented for the region 300-600°K.

There have been few studies of the thermal conductivity of diamond. The question has been considered in only a small number of Soviet and foreign articles. This is due to the methodological difficulties arising in thermophysical measurements on very small (∼1 mm) highly conductive specimens such as diamond crystals. We note that the thermal conductivity λ of pure nitrogen-free type IIa diamond crystals is 3-5 times that of copper at room temperature [1, 2].

Almost all known data on the thermal conductivity of diamond have been obtained with natural crystals of relatively large size and regular geometric form at low temperatures, while many practical applications of natural and synthetic diamonds require knowledge of thermal conductivity at moderate or high temperatures.

The present study will describe an experimental device for determination of the thermal conductivity of small diamond crystals 1 mm in size, of any geometric form, in the temperature range 300-600°K.

The operation of the device is based on a method described in [3] and utilized in [4] to determine the ratio of the thermal conductivity of type I and IIa natural diamonds to that of copper. The method is based on measurement of constriction thermal resistance [5], developed as a result of change in thermal flux when heat is transmitted into the specimen through an area whose radius is small in comparison to the linear dimensions of the specimen. The value of this resistance is given by the formula

$$R_t = \frac{H}{\pi \lambda r}, \tag{1}$$

where H is a dimensionless function, the value of which depends on the ratio between linear specimen dimensions and the radius of the area through which heat is introduced r. For specimens with dimensions (h, height; a, radius) satisfying the condition $h \simeq a > 10r$ the value

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