STEADY DIFFUSION IN LIQUID ACCOMPANIED BY CHEMICAL INTERACTION BETWEEN THE COMPONENTS

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Approximate matrix equations of the kinetics of nonequimolar mass transfer accompanied by chemical reaction between the components through a moving liquid film are obtained.

In practice, processes of mixture separation complicated by chemical reaction between components are encountered [1, 2]. The modeling of mass transfer in multiphase chemically active systems is complicated to a considerable extent because of the presence of reactions occurring in the liquid phase.

Mass transfer in multicomponent nonideal liquid mixtures is currently described using generalized Stefan—Maxwell equations in matrix form [3]. With nonequimolar mass transfer, the component fluxes may be determined from a difference scheme [4, 5], which allows the linearized matrix diffusion equation to be transformed to a system of independent scalar equations in terms of pseudocomponents. Therefore, the differential equations of nonequimolar diffusion of pseudocomponents for the physical model of mass transfer under consideration are solved by methods developed for binary mixtures [6]. Then, by means of inverse transformation, a general matrix form of the kinetic equation of mass transfer may be obtained.

Below, matrix equations are derived for calculating the molar fluxes of individual components through the boundary surfaces of a motionless film of chemically active liquid.

Consider the steady mass-transfer process at constant temperature and pressure in an n-component liquid mixture from the core of the phase to the phase boundary. It is assumed that, in diffusion through a thin liquid film of thickness δ forming at the phase interface, all the components enter into chemical reaction. Then the material-balance equation for the components may be written in the form

$$\frac{dN_i}{dz} = r_i, \quad i = 1, 2, \ldots, n,$$ (1)

where

$$N_i = J_i + x_i N_t;$$ (2)

$$\sum_{i=1}^{n} J_i = 0.$$ (3)

Equations (2) and (3) establish a relation between the total fluxes N_i relative to the motionless reference frame and the diffusional fluxes J_i relative to a reference frame moving at the mean molar velocity. With equimolar mass transfer, the total mass flux of the mixture $N_t = 0$. If there is no chemical reaction, the reaction rate $r_i = 0$, and the fluxes N_i are constant over the film thickness.

In accordance with the generalized Stefan—Maxwell equation, the following relation may be written [3]

$$(J) = -c [D_x] \frac{d(x)}{dz},$$ (4)

where

$$[D_x] = [A]^{-1} [\Gamma];$$ (5)

$$c = \frac{1}{\sum\limits_{i=1}^{n} x_i V_i}. \tag{6}$$

The elements of the matrix [A] and the thermodynamic-factor matrix [Γ] are determined from the formulas

$$\Gamma_{ij} = \delta_{ij} + \frac{x_i}{x_j} \frac{\partial \ln \gamma_i}{\partial \ln x_j}, \quad i, j = 1, 2, \ldots, n-1; \tag{7}$$

$$A_{ii} = \frac{x_i}{D_{in}} + \sum\limits_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_j}{D_{ij}}, \quad i = 1, 2, \ldots, n-1; \tag{8}$$

$$A_{ij} = x_i \left(\frac{1}{D_{in}} - \frac{1}{D_{ij}} \right), \quad i, j = 1, 2, \ldots, n-1, \; i \neq j. \tag{9}$$

The quantities $D_{ij} = D_{ji}$, $i, j = 1, 2, \ldots, n-1$, $i \neq j$, may be estimated from the molecular-diffusion coefficients of binary mixtures [7]. The elements of matrix $[D_x]$ are often calculated using the method of [8], which is based on the principle of corresponding states. Usually in practical calculations, the matrix $[D_x]$ and the total mixture density c are calculated from the mean composition and taken to be constant.

Substituting Eq. (4) into Eq. (2) and differentiating the result with respect to z, an (n − 1)-dimensional matrix equation is obtained

$$\frac{d(N)}{dz} = -c[D_x] \frac{d^2(x)}{dz^2} + \frac{dN_t}{dz}(x) + N_t \frac{d(x)}{dz}, \tag{10}$$

whose solution demands a knowledge of the specific dependence of the chemical reaction rates on the mixture composition.

Many chemical processes from beginning to end and most over some small interval may be satisfactorily described by linear systems in the form of monomolecular or pseudomolecular reactions, proceeding for a three-component mixture, for example, by the scheme [9]

$$A_1 \underset{k_{12}}{\overset{k_{21}}{\rightleftarrows}} A_2$$
$$A_2 \underset{k_{23}}{\overset{k_{32}}{\rightleftarrows}} A_3$$
$$A_3 \underset{k_{31}}{\overset{k_{13}}{\rightleftarrows}} A_1. \tag{11}$$

For a reaction of the type (11)

$$\sum\limits_{i=1}^{n} \frac{dN_i}{dz} = \sum\limits_{i=1}^{n} r_i = 0. \tag{12}$$

It follows from Eq. (12) that the overall molar flux of the mixture is independent of z:

$$\sum\limits_{i=1}^{n} N_{Ii} = \sum\limits_{i=1}^{n} N_{bi} = \sum\limits_{i=1}^{n} N_i = N_t = \text{const.} \tag{13}$$

The kinetic equations of the chemical reactions occurring according to the scheme in (11) may be written in (n − 1)-dimensional matrix form

$$(r) = c[K](x) + c(q), \tag{14}$$

where the elements of the square matrix [K] and column (q) are determined from the formulas

$$K_{ii} = -\sum\limits_{\substack{j=1 \\ j \neq i}}^{n} k_{ji} - k_{in}, \quad i = 1, 2, \ldots, n-1; \tag{15}$$

$$K_{ij} = k_{ij} - k_{in}, \quad i, j = 1, 2, \ldots, n-1, \; i \neq j; \tag{16}$$

$$q_i = k_{in}, \quad i = 1, 2, \ldots, n-1. \tag{17}$$

The matrix [K] is a nondegenerate matrix, the roots of whose characteristic equation are always less than zero [10].

The equation of nonequimolar diffusion — Eq. (10) — is written in the following form, taking account of Eqs. (1), (13), and (14)

$$-c\,[D_x]\frac{d^2(x)}{dz^2} + N_t\frac{d(x)}{dz} - c\,[K](x) = c\,(q).$$ (18)

The conditions under investigation, in which linear Eq. (18) contains two nondiagonal matrices of kinetic coefficients $[D_x]$ and $[K]$ in the general case, may be transformed to a system of independent scalar equations.

The matrix $[D_x]$ the roots of whose characteristic equation are different, may always be reduced to diagonal form using the matrix of intrinsic directions $[P]$ [4]:

$$[P]^{-1}[D_x][P] = \ulcorner D_x^0 \lrcorner.$$ (19)

The characteristic numbers D_{xi}^0 are larger than zero.

In the coordinate system defined by the linear transformation

$$(x') = [P]^{-1}(x),$$ (20)

Eq. (18) is rewritten in the following form, taking account of Eq. (19)

$$-c\,\ulcorner D_x^0 \lrcorner\frac{d^2(x')}{dz^2} + N_t\frac{d(x')}{dz} - c\,[KP](x') = c\,[P]^{-1}(q),$$ (21)

where

$$[KP] = [P]^{-1}[K][P].$$ (22)

The characteristic polynomial of the matrix is unchanged in all nonsingular transformations of the coordinate system

$$\det\{[P]^{-1}[K][P] - K^0\ulcorner I\lrcorner\} = \det\{[K] - K^0\ulcorner I\lrcorner\}.$$ (23)

Therefore, the characteristic numbers of the matrix $[KP]$ are equal to the characteristic numbers of the matrix $[K]$, and the matrix $[KP]$ may always be reduced to diagonal form

$$[R]^{-1}[KP][R] = \ulcorner K^0 \lrcorner$$ (24)

using the matrix of intrinsic directions $[R]$. Introducing the second auxiliary coordinate system

$$(x'') = [R]^{-1}(x'),$$ (25)

Eq. (21) is rewritten, taking account of Eq. (24)

$$-c\,[R]^{-1}\ulcorner D_x^0 \lrcorner[R]\frac{d^2(x'')}{dz^2} + N_t\frac{d(x'')}{dz} - c\,\ulcorner K^0 \lrcorner(x'') = c\,(q''),$$ (26)

where

$$(q'') = [R]^{-1}[P]^{-1}(q).$$ (27)

Hence it follows that the matrix equation of nonequimolar multicomponent diffusion with chemical reaction — Eq. (18) — for the general case of mass transfer cannot be written in the form of a system of independent scalar equations, since the characteristic numbers D_{xi}^0 are different, and $[R]$ is a nondiagonal matrix. This representation is possible if the following condition is satisfied with good approximation

$$[R]^{-1}\ulcorner D_x^0 \lrcorner[R] \approx \ulcorner D_m \lrcorner,$$ (28)

i.e., when the cross coefficients of the square matrix $[R]^{-1}\ulcorner D_{xi}^0 \lrcorner[R]$ may be neglected.

The approximate solution is written on the assumption that Eq. (28) holds. Then diffusion with a chemical reaction may be described by a system of independent equations

$$-\beta_{xi}^0\frac{d^2x_i''}{d\eta^2} + N_t\frac{dx_i''}{d\eta} - c^2\frac{D_{mi}K_i^0}{\beta_{xi}^0}x_i'' = c^2\frac{D_{mi}}{\beta_{xi}^0}q_i'',$$ (29)

$$i = 1,\ 2,\ \dots,\ n-1,$$

with the boundary conditions

when $z = 0$ $\eta = 0$, core of phase $(x'') = (x_b'')$;

when $z = \delta$ $\eta = 1$, phase boundary, $(x'') = (x_l'')$. (30)

In the latter equations, the mass-transfer coefficients of the individual components are introduced

$$\beta_{xi}^0 = \frac{cD_{mi}}{\delta}, \quad i = 1, 2, \ldots, n-1,$$ (31)

which may be determined from the criterial equation of binary mixtures. Equation (31) is physically meaningful if all the coefficients D_{mi} are larger than zero. When this requirement is satisfied, the characteristic equation corresponding to any differential equation of the system in Eq. (29) has the real roots

$$\lambda_{i1,2} = \frac{\psi_i}{2} \pm \sqrt{\left(\frac{\psi_i}{2}\right)^2 + \xi_i},$$ (32)

where

$$\psi_i = \frac{N_t}{\beta_{xi}^0}, \quad \xi_i = -D_{mi}K_i^0\left(\frac{c}{\beta_{xi}^0}\right)^2.$$ (33)

Then each equation of the system in Eq. (29) with the boundary conditions in Eq. (30) has the following solution:

$$\left(x_i'' + \frac{q_i''}{K_i^0}\right) = \frac{1}{e^{\lambda_{i2}} - e^{\lambda_{i1}}}\left[\left(x_{bi}'' + \frac{q_i''}{K_i^0}\right)(e^{\lambda_{i2} + \lambda_{i1}\eta} - e^{\lambda_{i1} + \lambda_{i2}\eta}) - \left(x_{Ii}'' + \frac{q_i''}{K_i^0}\right)(e^{\lambda_{i1}\eta} - e^{\lambda_{i2}\eta})\right],$$
$$i = 1, 2, \ldots, n-1.$$ (34)

The diffusional fluxes relative to the reference frame moving at the mean molar velocity through the boundary surfaces of the liquid film may be calculated from the expression

$$(J_{b,I}) = -c[D_x]\frac{d(x)}{dz}\Big|_{\substack{z=0 \\ z=\delta}},$$ (35)

or in the coordinates transformed according to Eqs. (20) and (25)

$$(J_{b,I}'') = -\lceil\beta_x^0\rfloor\frac{d(x'')}{d\eta}\Big|_{\substack{\eta=0 \\ \eta=1}}.$$ (36)

The subscript b denotes the diffusional flux through the surface corresponding to the dimensionless coordinate $\eta = 0$ (the core of the phase) the subscript I denotes $\eta = 1$ (the boundary of the immiscible phases).

Differentiating Eq. (34) with respect to η and determining the gradients in Eq. (36), the expression for $(J_{b,I}'')$ is written in the form

$$(J_{b,I}'') = \lceil\beta_x^0\rfloor\lceil f_{b,I}\rfloor\{(x_b'') - \lceil K^0\rfloor^{-1}(q'')\} - \lceil\beta_x^0\rfloor\lceil h_{b,I}\rfloor\{(x_I'') - \lceil K^0\rfloor^{-1}(q'')\}.$$ (37)

In calculating the flux through the phase boundary (J_I''), the elements of the diagonal matrices $\lceil f_I \rfloor$ and $\lceil h_I \rfloor$ are calculated from the formulas

$$f_{Ii} = \frac{b_i}{\operatorname{sh} b_i}\exp\left(\frac{\psi_i}{2}\right), \quad i = 1, 2, \ldots, n-1;$$ (38)

$$h_{Ii} = \frac{\psi_i}{2} + b_i\frac{\operatorname{ch} b_i}{\operatorname{sh} b_i}, \quad i = 1, 2, \ldots, n-1,$$ (39)

where

$$b_i = \sqrt{\left(\frac{\psi_i}{2}\right)^2 + \xi_i},$$ (40)

and the expressions used for (J_b'') are

$$f_{bi} = -\frac{\psi_i}{2} + b_i\frac{\operatorname{ch} b_i}{\operatorname{sh} b_i}, \quad i = 1, 2, \ldots, n-1;$$ (41)

$$h_{bi} = \frac{b_i}{\operatorname{sh} b_i}\exp\left(-\frac{\psi_i}{2}\right), \quad i = 1, 2, \ldots, n-1.$$ (42)

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Inverse transformation from the transformed physical quantities to the natural physical quantities by means of Eqs. (20) and (25) allows the mass-transfer equation to be written in the form

$$(J_{b,I}) = [\beta_{b,I}]\{(x_b) + [K]^{-1}(q)\} - [\beta_b^*{}_{,I}]\{(x_I) + [K]^{-1}(q)\}. \tag{43}$$

In Eq. (43), the square matrices of mass-transfer coefficients in the liquid are calculated from the formulas

$$[\beta_{b,I}] = [P][R]\ulcorner\beta_x^0\lrcorner\ulcorner f_{b,I}\lrcorner[R]^{-1}[P]^{-1}, \tag{44}$$

$$[\beta_b^*{}_{,I}] = [P][R]\ulcorner\beta_x^0\lrcorner\ulcorner h_{b,I}\lrcorner[R]^{-1}[P]^{-1}. \tag{45}$$

In accordance with Eqs. (43)-(45), the rate of nonequimolar mass transfer in the phase is characterized by two square matrices of mass-transfer coefficients. Because of the difference in the parameters f_i and h_i, these matrices are not equal. The rate of mass transfer without chemical reaction is characterized by a single matrix of kinetic coefficients. It is simple to show that, when $r_i = 0$, $i = 1, 2,...,n$, Eq. (43) written for the fluxes through the surface when $\eta = 0$, for example, transforms to the form

$$(J_b) = [\beta](x_b - x_I), \tag{46}$$

where

$$[\beta] = [P]\ulcorner\beta_x^0\lrcorner\ulcorner f_b\lrcorner[P]^{-1}, \tag{47}$$

$$f_{bi} = h_{bi} = \frac{\psi_i}{\exp\psi_i - 1}, \quad i = 1, 2, ..., n-1, \tag{48}$$

which is the accurate solution of the nonequimolar-diffusion Eq. (10) for the film model [11].

With nonequimolar mass transfer, the fluxes of the components relative to the motionless reference frame are always calculated using iterative algorithms since the transfer coefficients according to Eqs. (38)-(42), (44), and (45) depend on the total mole flux of the mixture N_t. Equation (43) is solved together with Eqs. (2) and (13). First the fluxes through the phase boundary N_{Ii} are found by methods of simple iteration, and then N_t and N_{bi} are determined. The components for which the phase boundary is impermeable must be known here. The algorithm for numerical solution of the analogous problem was described in [11].

The assumption in Eq. (28) limits the region of application of the model in Eq. (43). The elements of the square matrix $[R]^{-1}\ulcorner D_x^0\lrcorner[R]$ must be estimated preliminarily from Eqs. (5)-(9), (15)-(17), (19), (22), and (24) and its structure must be investigated, which is associated with a sufficiently large volume of computational work. However, it would be expected that this assumption would be acceptable for many mixtures that are separable industrially, since the diffusional interaction between the components in the liquid is often slight and may be neglected [8, 12]. In this case, $D_m = D_{xi}$, $i = 1, 2,...,n - 1$. For example, in [8], the matrix $[D_x]$ was calculated for a significantly nonideal ternary mixture consisting of materials that differ strongly in physical properties. The results of the calculation show, on comparison with experimental data, that $[D_x]$ is close to a diagonal matrix with equal elements.

NOTATION

x, concentration of component in liquid; N, flux of material relative to motionless reference frame; J, flux of material relative to the reference frame moving at the mean molar velocity; N_t, total flux of mixture; r, rate of chemical reaction with respect to the component; V, molecular volume of the pure component; γ, activity coefficient; k, rate constant of chemical reaction; D_x^0, characteristic number of $[D_x]$; K^0, characteristic number of $[K]$; c, total molar density of mixture; δ, thickness of gas film; z, coordinate of diffusional path length; η, dimensionless coordinate of diffusional path length; β_x^0, mass-transfer coefficient; δ_{ij}, Kronecker delta; [ ], square matrix; $\ulcorner\lrcorner$, diagonal matrix; ( ), column matrix; i, j, component numbers; n, number of components; I, phase boundary; b, core of liquid phase.

LITERATURE CITED

1. G. Kaibel, H. H. Mayer, and B. Seid, "Reaktionen in Distillationskolonnen," Chem. Ing. Tech., 50, No. 8, 586-592 (1978).

2. E. E. Frolovskii, V. B. Kogan, and V. V. Zyryanov, "Mathematical description of the separation of a multicomponent ideal mixture accompanied by chemical reaction," Teor. Osn. Khim. Tekhnol., 6, No. 4, 572-578 (1972).
3. R. Krishna, "Steady-state mass transport in multicomponent liquid mixtures," Lett. Heat Mass Transfer, 3, 153-162 (1976).
4. H. L. Toor, "Solution of the linearized equations of multicomponent mass transfer: matrix methods," AIChE J., 10, No. 4, 460-465 (1964).
5. W. E. Stewart and R. Prober, "Matrix calculation of multicomponent mass transfer in isothermal systems," Ind. Eng. Chem. Fundam., 3, No. 3, 224-235 (1964).
6. R. B. Bird et al., Nuclear Transport [Russian translation], Khimiya, Moscow (1974).
7. E. L. Cussler, Multicomponent Diffusion, Elsevier, Amsterdam (1976).
8. A. N. Planovskii, V. N. Mazaev, and A. I. Katalov, "Molecular-diffusion coefficients in multicomponent liquid mixtures," Teor. Osn. Khim. Tekhnol., 9, No. 5, 755-758 (1975).
9. A. A. Bezdenezhnykh, Engineering Methods of Comparing Reaction-Rate Equations and Calculating Kinetic Constants [in Russian], Khimiya, Leningrad (1973).
10. L. E. Johns and X. B. Reed, "On diffusion reaction interference in heterogeneous chemical reaction systems," Chem. Eng. Sci., 29, No. 1, 288-290 (1974).
11. R. Krishna and G. L. Standart, "A multicomponent film model incorporating a general matrix method of solution to the Maxwell—Stefan equations," AIChE J., 22, No. 2, 383-389
12. A. I. Katalov, V. S. Nikitin, and A. N. Planovskii, "Modeling mass-transfer kinetics in multicomponent mixtures," Teor. Osn. Khim. Tekhnol., 14, No. 5, 672-677 (1980).

HEAT-EXCHANGE CRISIS IN THERMOSIPHON CIRCUITS

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The article discusses the analogy and distinguishing features of heat-exchange crises in steam-generating channels of thermosiphon circuits. A chart of the crisis phenomena in channels with natural and forced circulation is presented.

At present various designs of two-phase thermosiphons operating on the principle of closed circulation circuits are widely used. Determining the limits within which these devices are able to operate requires studying the conditions under which heat-exchange crisis originate in two-phase streams with natural circulation of the working medium. Although there is a great variety of applications of the above-mentioned method of circulation, the problem of heat-exchange crises under the given conditions has been studied quite insufficiently.

It is currently assumed that in circuits with natural circulation of the heat-transfer agent (analogously to the case of forced motion) the critical thermal loads have not only to be limited by crises of boiling of the first kind but also by crises of heat exchange of the second kind which are connected with the complete evaporation of the liquid film next to the wall. In addition, the known results of investigations of crises of heat exchange in vaporizer circuits and evaporators indicate that there are considerable quantitative differences between the regularities of crisis phenomena under the given conditions; this is explained by a number of authors by the existence of vibrational instability and low-frequency pulsations in the circuit. The available experimental data on crises of heat exchange in thermosiphons with internal down channel also indicate that the pattern of crisis phenomena is a complex one.

A promising direction in the solution of the above problem may apparently be the successive study of the conditions of the onset of crisis phenomena in the simplest circuits with free convection and their comparison with the basic research of these phenomena under conditions of forced motion. At the first stage it is important to have reliable experimental results on crises of heat exchange where circuits with natural circulation operate in regimes