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Solution of the Linearized Equations of Multicomponent Mass Transfer:

II. Matrix Methods

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Solutions to the equations of multicomponent mass transfer may be written as matrix generalizations of the solution to the equivalent binary mass transfer equation when initial and boundary concentrations are constant, there are no homogeneous reactions, and all physical properties including the diffusion coefficient matrix are concentration independent.

The analogue of the binary mass transfer coefficient is a multicomponent mass transfer coefficient matrix which depends only upon the mass transfer coefficients of the equivalent binary system and the diffusion coefficient matrix of the multicomponent system.

When interphase transfer takes place, the inverse multicomponent mass transfer coefficient matrices of each phase are additive. Their sum yields an overall resistance to mass transfer which is the inverse of the overall multicomponent mass transfer coefficient matrix.

GENERAL THEORY

In Part I the linearized equations of multicomponent mass transfer were uncoupled, and solutions were obtained by an algebraic method.

In this part matrix methods are used to carry out the analysis. The present method is more efficient for systems of more than three components, gives solutions even if the diffusion equations cannot be uncoupled, and is advantageous in considering transfer between phases.

The starting equations for an $n + 1$ component system may be written as (*6*)

$$\frac{\partial C_i}{\partial \theta} + \nabla \cdot \{\underline{V}\, C_i\} = - \nabla \cdot \underline{j}_i + r_i, \; i = 1, .., n \qquad (1')$$

$$\underline{j}_i = - \sum_j D_{ij} \nabla C_j, \; i = 1, .., n \qquad (2')$$

and summations are always from 1 to n. A primed equation number indicates the scalar form of a matrix equation which will be written with the same number. The flux with respect to a coordinate moving at the reference velocity $\underline{V}$ has been written separately here to emphasize the fact that it is the coupling in Equation (2′) which gives rise to the basic difference between binary and multicomponent systems.

If the C_i are written as the elements of a column vector (C), the concentration vector; the $\underline{j}_i$ as the elements of a column vector $(\underline{j})$, the flux vector; the r_i as the elements of a column vector (r), the reaction vector; and the D_{ij} as the elements of a matrix $[D]$, the diffusion coefficient matrix; then in matrix notation Equations (1′) and (2′) become

$$\frac{\partial (C)}{\partial \theta} + \nabla \cdot \{\underline{V}(C)\} = - \nabla \cdot (\underline{j}) + (r) \qquad (1)$$

$$(\underline{j}) = - [D](\nabla C) \qquad (2)$$

It is noted that on thermodynamic grounds when all the n independent concentration gradients are zero all the n independent fluxes must be zero, and vice-versa. Hence $[D]$ must be nonsingular.

Equations (1) and (2) are now partially linearized as before (*6*) by assuming that the matrix $[D]$, which in

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general is concentration dependent, may be treated as concentration independent. (The reaction term may still be nonlinear in concentration.) Although the results obtained by this procedure will only be exact for vanishingly small changes in concentration, there are indications (6) that the errors caused by the assumption are not serious even for moderate concentration changes.

Assume that $[D]$ may be diagonalized by a nonsingular matrix $[t]$:

$$[t]^{-1}\,[D]\,[t] = \begin{bmatrix} D_1 & & & \\ & D_2 & & \\ & & \ddots & \\ & & & D_n \end{bmatrix} \tag{3}$$

Then operating on Equation (2) by $[t]^{-1}$ and using Equation (3) one gets

$$(\underline{\epsilon}) = -\begin{bmatrix} D_1 & & & \\ & D_2 & & \\ & & \ddots & \\ & & & D_n \end{bmatrix} (\nabla\psi) \tag{4}$$

where

$$(\underline{\epsilon}) = [t]^{-1}\,(\underline{j}) \tag{5}$$

$$(\psi) = [t]^{-1}\,(C) \tag{6}$$

Equation (4) represents the set of uncoupled scalar equations

$$\underline{\epsilon_k} = -\,D_k\,\nabla\,\psi_k, \quad k = 1, .., n \tag{4'}$$

each of which is identical in form to the usual binary equation.

Operating on Equation (1) by $[t]^{-1}$ one obtains

$$\frac{\partial(\psi)}{\partial\theta} + \nabla\cdot\{\underline{V}(\psi)\} = -\,\nabla\cdot(\underline{\epsilon}) + (R) \tag{7}$$

where

$$(R) = [t]^{-1}\,(r) \tag{8}$$

Hence it is seen that when Equation (2) can be reduced to Equation (4), combination of Equations (4) and (7) gives

$$\frac{\partial(\psi)}{\partial\theta} + \nabla\cdot\{\underline{V}(\psi)\} = \begin{bmatrix} D_1 & & & \\ & D_2 & & \\ & & \ddots & \\ & & & D_n \end{bmatrix} \nabla^2(\psi) + (R) \tag{9}$$

which represents the set of scalar diffusion equations

$$\frac{\partial\psi_k}{\partial\theta} + \nabla\cdot\{\underline{V}\,\psi_k\} = D_k\,\nabla^2\,\psi_k + R_k, \quad k = 1, .., n \tag{9'}$$

each of which has the form of the binary diffusion equation. Equation (9′) was obtained earlier (6).

For the sake of completeness the equation in terms of the fluxes with respect to a fixed coordinate are also given. Define $(\underline{N})$ as the column vector whose elements are $\underline{N_i}$ so that

$$(\underline{N}) = (\underline{j}) + \underline{V}\,(C) \tag{10}$$

Equation (1) may be written as

$$\frac{\partial(C)}{\partial\theta} + \nabla\cdot(\underline{N}) = (r) \tag{11}$$

Operating with $[t]^{-1}$ as before one gets

$$\frac{\partial(\psi)}{\partial\theta} + \nabla\cdot(\underline{\eta}) = (R) \tag{12}$$

where

$$(\underline{\eta}) = [t]^{-1}(\underline{N}) = (\underline{\epsilon}) + \underline{V}(\psi) \tag{13}$$

and

$$(\underline{\eta}) = -\begin{bmatrix} D_1 & & & \\ & D_2 & & \\ & & \ddots & \\ & & & D_n \end{bmatrix} (\nabla\,\psi) + \underline{V}(\psi) \tag{14}$$

or

$$\underline{\eta_k} = -\,D_k\,\nabla\psi_k + \underline{V}\,\psi_k, \quad k = 1, .., n \tag{14'}$$

which is identical in form to the usual binary diffusion equation. Equation (14′) was obtained earlier (6).

Thus if the diffusion coefficient matrix $[D]$ can be diagonalized, the coupled equations of multicomponent mass transfer can be reduced to a set of equations which are uncoupled in the diffusion terms and which describe the diffusion of n linear combinations of the n independent components. Each linear combination (combine) diffuses as if it were a component of a binary mixture in which the diffusion coefficient is D_k, the rate of reaction is R_k, and the reference velocity is V. Hence solutions to multicomponent problems may be obtained in terms of solutions to equivalent binary problems. In many cases of interest the set of equivalent binary problems is easily identified, but at times it is not and at times the equivalent binary problem set may not correspond to any real binary system. These points were discussed in Part I.

Because $[D]$ is nonsymmetrical, if there are repeated roots it may or may not be possible to find a nonsingular $[t]$ which diagonalizes $[D]$.[2]* In all situations examined so far (ternary liquids and gases) the roots have been distinct, so $[t]$ is nonsingular (this is equivalent to the condition in Part I that $s_{ik} \neq 0$). It will be shown later that solutions to the diffusion equations may be obtained even in the exceptional cases in which $[D]$ cannot be diagonalized.

The combine diffusion coefficients are the characteristic roots (eigenvalues) of $[D]$ which are obtained by solving the characteristic equation of $[D]$ (2, 3). The equivalent result was obtained earlier (6). Although there are n roots of the characteristic equation, some may be repeated. The real parts of the roots must be positive if the method is to be valid. So far no cases of negative (or complex) roots have been found in gases or in liquids.* (Zero roots are ruled out because $[D]$ is nonsingular.)

Since the eigenvectors of $[D]$, the columns of $[t]$, are fixed only to within an arbitrary multiplying constant, each combine concentration and flux is also fixed only to within an arbitrary constant.

The results obtained so far are essentially those obtained earlier (6). In the earlier method the multiplying constant on the combines was fixed, and the cofactors of the t_{ik} were evaluated rather than the t_{ik} themselves.

CONCENTRATION PROFILES

Consider a nonreacting n plus 1 component mixture with constant physical properties and with a prescribed velocity field such that $\nabla\cdot\underline{V} = 0$. Each component is assumed to have a constant initial concentration C_{io}, and at time zero the concentration of each component at some boundary B is assumed to change to C_i^*, a constant. At some other boundary b the flux of every component is zero and $\underline{V}$ is zero. Hence from Equation (1) the equation to be solved is

$$\left\{ \frac{\partial}{\partial\theta} + \underline{V}\cdot\nabla \right\} (C) = [D]\,\nabla^2(C) \tag{15}$$

with the boundary conditions

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* H. T. Cullinan, Jr., has since shown, in a paper to be published, that if the Onsager reciprocal relationships are valid, the system is thermodynamically stable, and the volume reference frame is used, then the characteristic roots are real positive numbers and [t] is nonsingular.

$$(\Delta C(x, y, z, 0)) = (C_o) - (C^*) = (\Delta C_o) \qquad (15a)$$

$$(\Delta C(B, \theta)) = 0 \qquad (15b)$$

$$\left(\frac{\partial C(b, \theta)}{\partial S}\right) = 0 \qquad (15c)$$

The last relationship follows from the zero flux condition because $[D]$ is nonsingular.

In order to solve these equations the equations are transformed as before to obtain the uncoupled scalar equations

$$\left\{ \frac{\partial}{\partial \theta} + \underline{V} \cdot \nabla \right\} \psi_k = D_k \nabla^2 \psi_k \qquad (16')$$

$$\Delta\psi_k(x, y, z, 0) = \sum_j \frac{T_{jk}\,\Delta C_{jo}}{|t|} = \Delta\psi_{ko} \qquad (16'a)$$

$$\Delta\psi_k\,(B, \theta) = 0 \qquad (16'b)$$

$$\frac{\partial\,\psi_k(b, \theta)}{\partial S} = 0 \qquad (16'c)$$

for $k = 1, \ldots, n$.

Equation (16′) represents a set of equivalent binary problems whose solution may be written as

$$\Delta\psi_k = f(D_k, x, y, z, \theta)\,\Delta\psi_{ko}, \quad k = 1, \ldots, n \qquad (17')$$

where the solution function f satisfies the equation

$$\left\{ \frac{\partial}{\partial \theta} + \underline{V} \cdot \nabla \right\} f(D_k, \ldots) = D_k \nabla^2 f(D_k, \ldots) \qquad (18)$$

and the boundary conditions

$$f(D_k, x, y, z, 0) = 1 \qquad (18a)$$

$$f(D_k, B, \theta) = 0 \qquad (18b)$$

$$\frac{\partial f(D_k, b, \theta)}{\partial S} = 0 \qquad (18c)$$

for $k = 1, \ldots, n$.

Equation (17′) in matrix notation is

$$(\Delta\psi) = \begin{bmatrix} f_1(D_1) & & & \\ & f(D_2) & & \\ & & \cdot & \\ & & & f(D_n) \end{bmatrix} (\Delta\psi_o) \qquad (17)$$

where the space and time variables are not written explicitly any more since they are the same for each combine. The solution to Equation (15 in terms of (C) is now obtained by first inverting Equation (6) and then using Equation (17) to give

$$(\Delta C) = [f]\,(\Delta C_o) \qquad (18)$$

where $[f]$, the solution matrix, is given by

$$[f] = [t] \begin{bmatrix} f(D_1) & & & \\ & f(D_2) & & \\ & & \cdot & \\ & & & f(D_n) \end{bmatrix} [t]^{-1} \qquad (19)$$

$[D]$ and $[f]$ are closely related, since from Equation (3)

$$[D] = [t] \begin{bmatrix} D_1 & & & \\ & D_2 & & \\ & & \cdot & \\ & & & D_n \end{bmatrix} [t]^{-1} \qquad (20)$$

so the solution matrix $[f]$ is diagonalized by the similarity transformation which diagonalizes the diffusion coefficient matrix; $[D]$ and $[f]$ have the same modal matrices. Each characteristic root of $[f]$ at x, y, z, θ is $f(D_k)$, the reduced concentration profile of combine k at the same x, y, z, θ.

If f is an analytic function of D, it follows from Equations (19) and (20) (2, 3) that

$$[f] = f([D]) \qquad (21)$$

where $f([D])$ is given by Sylvester's theorem, but it will be seen that this result is also valid when f is not an analytic function of D and furthermore is valid even if $[D]$ cannot be diagonalized.

Hence the solution to Equation (15) is a direct generalization of the binary solution

$$(\Delta C) = f([D])\,(\Delta C_o) \qquad (22)$$

The expansion of $f([D])$ depends upon the nature of the roots D_k.

Characteristic Roots all Distinct

If the D_k are all distinct, Sylvester's theorem gives (2)

$$f([D]) = \sum_k f(D_k)\,[Z_o(D_k)] \qquad (23)$$

where

$$[Z_o(D_k)] = \frac{\prod\limits_{j \neq k} (D_j I - [D])}{\prod\limits_{j \neq k} (D_j - D_k)} \qquad (24)$$

The condition (2)

$$\sum_k [Z_o(D_k)] = I \qquad (25)$$

and Equations (18a), (18b), and (18c) show that Equation (22) with Equation (23) indeed satisfies the initial and boundary conditions, Equations (15a), (15b), and (15c). Further direct substitution of Equation (22) with $f([D])$ given by Equation (23) into Equation (15) and use of Equation (18) and the Cayley-Hamilton theorem (2) shows that the solution satisfies the original differential equation, Equation (15). Hence the solution is verified whether or not f is analytic.

The relationship between the present solution and that given earlier is obtained by writing Equation (22) in the expanded form

$$\Delta C_i = \sum_j f_{ij}\,\Delta C_{jo}, \quad i = 1, \ldots, n \qquad (26)$$

The f_{ij} were given in Part I in terms of the $f(D_k)$ and constants which had to be calculated for each value of n. In the present method the f_{ij} are obtained directly from Equation (23). A direct expansion of this Equation or use of the alternate form given by Pipes (3) yields

Three components

$$f_{ij} = \frac{D_{ij} - D_2\,\delta_{ij}}{D_1 - D_2} f(D_1) + \frac{D_{ij} - D_1\,\delta_{ij}}{D_2 - D_1} f(D_2) \qquad (27)$$

which essentially was obtained earlier (6).

Four components

$$\begin{aligned} f_{ij} = & \left\{ \frac{\sum_l D_{il} D_{lj} - (D_2 + D_3)\,D_{ij} + D_2 D_3\,\delta_{ij}}{(D_2 - D_1)(D_3 - D_1)} \right\} f(D_1) \\ & + \left\{ \frac{\sum_l D_{il} D_{lj} - (D_1 + D_3)\,D_{ij} + D_1 D_3\,\delta_{ij}}{(D_1 - D_2)(D_3 - D_2)} \right\} f(D_2) \\ & + \left\{ \frac{\sum_l D_{il} D_{lj} - (D_1 + D_2)\,D_{ij} + D_1 D_2\,\delta_{ij}}{(D_1 - D_3)(D_2 - D_3)} \right\} f(D_3) \end{aligned} \qquad (28)$$

It is seen that complete coupling exists; if any component is disturbed, all components are disturbed. Further discussion appears in Part I.

Repeated Roots

When there are repeated roots it may or may not be possible to diagonalize $[D]$, that is to reduce Equation (1) to the form of Equation (9). Even though no cases of repeated roots have been observed so far in ternary systems, they may still occur in ternary liquid mixtures or in mixtures of more than three components. If repeated roots do exist, they clearly will represent exceptional cases, but it is still of interest to examine the solution under these conditions.

With consideration of the earlier example it is still assumed that the solution to Equation (15) is given by Equation (22), but now Equation (23) is not valid. Rather the confluent form of Sylvester's theorem must be used to expand $f([D])$. This form is given by Frazer, Duncan, and Collar (2), but rather than repeating the general expansion a simple example is given.

If both roots in a ternary system are equal to D_1, the confluent form yields

$$[f] = f([D]) = f(D_1)I + ([D] - D_1 I)\left.\frac{\partial f(D)}{\partial D}\right|_{D=D_1} \tag{29}$$

Substitution of this equation into Equation (22), substitution of the result into Equation (15), and use of the Cayley-Hamilton theorem shows that the differential equation is satisfied. The boundary conditions are also satisfied since at boundary B and at time zero

$$\left.\frac{\partial f(D)}{\partial D}\right|_{D=D_1} = 0 \tag{30}$$

and at boundary b

$$\frac{\partial}{\partial S}\left.\frac{\partial f(D)}{\partial D}\right|_{D=D_1} = \frac{\partial}{\partial D}\left.\frac{\partial f(D)}{\partial S}\right|_{D=D_1} = 0 \tag{31}$$

Thus the solution to (15) when the two roots are equal is given by Equations (29) and (22). In expanded form the result is

$$\Delta C_i = \left\{ f(D_1) + (D_{ii} - D_1)\left.\frac{\partial f(D)}{\partial D}\right|_{D=D_1} \right\} \Delta C_{io} + D_{ij}\left.\frac{\partial f(D)}{\partial D}\right|_{D=D_1} \Delta C_{jo}, \quad \begin{matrix} i = 1, 2 \\ j \neq i \end{matrix} \tag{32}$$

It is noted that this same result can be obtained by taking the limit of Equation (27) [or more conveniently Equation (42), Part I] as $D_2 \rightarrow D_1$.

It is also noted that Equation (32) is valid whether or not $[D]$ may be diagonalized. In the trivial case of equal roots, $[D] - D_1 I = 0$, there is no coupling, and the diagonal form exists; but if the roots were equal with $[D] - D_1 I \neq 0$, then the diagonal form would not exist, but the last term in Equation (32) would remain, giving rise to coupling.

It can be shown in general that the confluent expansion of $f([D])$ satisfies the original differential equation as well as the boundary conditions. Hence the earlier assumptions that $[D]$ may be diagonalized and that f is analytic are not necessary.

Although Equation (22) is limited to constant initial and boundary concentrations, it includes problems other than the one stated, steady forced convection for example. It is generally valid when the equivalent binary problem can be written in the form of Equation (17').

The method holds for a wider class of problems however. If Equation (17') is replaced by

$$\Delta\psi_k = f_1(D_k, x, y, z, \theta)\,\Delta\psi_{k1} + f_2(D_k, x, y, z, \theta)\,\Delta\psi_{k2}, \quad k = 1, \ldots, n \tag{33}$$

then the multicomponent solution is

$$(\Delta C) = f_1([D])(\Delta C_1) + f_2([D])\,\Delta C_2 \tag{34}$$

As before the space and time variables are not written explicitly. This might be the problem in which the concentrations at boundary b are all held constant.

TRANSFER RATES

Low Fluxes

The rates of mass transfer may be obtained from the mass transfer coefficients which correspond to the equivalent binary problem (as was done in Part I). When $[D]$ can be diagonalized, Equation (1) reduces to the binary form [Equations (9) and (14)], and if there are no homogeneous reactions, the rate of transfer of each combine across the interface is given by

$$(\eta_I) = \begin{bmatrix} k(D_1) & & & \\ & k(D_2) & & \\ & & \cdot & \\ & & & \cdot \\ & & & & k(D_n) \end{bmatrix} (\Delta\psi_o) \tag{35}$$

where $k(D_i)$ is the ordinary binary mass transfer coefficient when the binary diffusion coefficient is D_i and $(\Delta\psi_o) \equiv (\psi_I) - (\overline{\psi})$. It is assumed as before that the initial and boundary concentrations are constants. When the normal component of the reference velocity at the interface is zero or small, k is independent of this velocity and may also be taken as independent of the concentrations. In general however k varies with position, hydrodynamics, etc.

Converting to component concentrations by use of Equations (6) and (13) one gets

$$(N_I) = [k]\,(\Delta C_o) \tag{36}$$

where $[k]$ is the multicomponent mass transfer coefficient matrix given by

$$[k] = [t]\begin{bmatrix} k(D_1) & & & \\ & k(D_2) & & \\ & & \cdot & \\ & & & \cdot \\ & & & & k(D_n) \end{bmatrix}[t]^{-1} \tag{37}$$

The elements of $[k]$, k_{ij}, have been defined (6) as the multicomponent mass transfer coefficients with the diagonal terms the main coefficients and the off-diagonal terms the cross coefficients. The definition follows from Equations (37) and (20). $[k]$ is related to $[D]$ through the binary mass transfer coefficient in the same way that $[f]$ is related to $[D]$ through the binary solution function.

Equations (37) and (20) indicate that

$$[k] = k([D]) \tag{38}$$

and if the D_k are distinct

$$[k] = k([D]) = \sum_k k(D_k)\,[Z_o(D_k)] \tag{39}$$

If there are repeated roots, $k([D])$ is given by the confluent form of Sylvester's theorem whether or not $[D]$ may be diagonalized. These results are confirmed (whether or not k and f are analytic) by the relationship [obtained if (ΔC_o) is chosen properly]

$$[k] = -[D]\left.\frac{\partial f([D])}{\partial S}\right|_I \tag{40}$$

which shows that if the expansion of $f([D])$ is valid so is the expansion of $k([D]$.

Hence the multicomponent rate equation is

$$(N_I) = k([D]\,(\Delta C_o) \tag{41}$$

a direct generalization of the binary rate equation.

Examples of the expanded form of $[k]$ may be obtained from those given earlier for $[f]$ by replacing f_{ij} by k_{ij} and $f(D_i)$ by $k(D_i)$.

Moderate Fluxes

When the normal component of the reference velocity at the interface cannot be neglected, Equation (35) may still be used, but $k(D_i)$ must be replaced by a form like $k(D_i, v_I, \psi_{iI}, \bar{\psi}_i)$ which is defined as k_i. Now the k_i depend upon the concentrations and the reference velocity at the interface as well as upon D_i, and the functional form is the same as in the equivalent binary problem.

It will still frequently be convenient to use Equation (36), but now because the diagonal elements in Equation (37) depend upon other quantities in addition to the diffusion coefficients Equation (39) becomes ambiguous.

This ambiguity can be removed if the D_i and k_i are distinct. Assume that the k_i are given. It is now necessary to evaluate the matrix $[k]$ from the expression

$$[t]^{-1}\,[k]\,[t] = \begin{bmatrix} k_1 & & & & \\ & k_2 & & & \\ & & \cdot & & \\ & & & \cdot & \\ & & & & k_n \end{bmatrix} \tag{42}$$

To do this assume the expansion

$$[k] = a_0 I + a_1[D] + \ldots a_{n-1}[D]^{n-1} \tag{43}$$

where the a_i are scalar coefficients to be determined (in general at each time and position). Substituting Equation (43) into (42) and carrying out the similarity transformation on each term one obtains a set of n simultaneous linear equations which can be solved for the a_i. The result is the same as an equation given by Pipes (*4*)

$$a_r = \frac{A_r}{A} \tag{44}$$

where A is the determinant

$$A = \begin{vmatrix} 1 & 1 & \ldots 1 \\ D_1 & D_2 & \ldots D_n \\ \cdot & \cdot & \ldots\cdot \\ D_1{}^{n-1} & D_2{}^{n-1} & \ldots D_n{}^{n-1} \end{vmatrix} \tag{45}$$

and A_{r-1} is derived from A by replacing the elements of the rth row by $k_1, k_2, \ldots\ldots\ldots k_n$. Equation (43) may then be directly used to evaluate $[k]$ or may be used to show that Equation (39) is now replaced by

$$[k] = \sum_k k_k\,[Z_o(D_k)] \tag{46}$$

Hence the earlier scalar expansions for $[f]$ hold if f_{ij} is replaced by k_{ij} and $f(D_i)$ by k_i. The k_i of course will generally have to be evaluated by trial and error.

An alternate treatment of the high flux problem is to use the Stewart mass transfer coefficients (*1*) in place of the earlier ones so that Equation (35) is replaced by

$$(\eta_I) = \begin{bmatrix} \dot{k}(D_1) & & & & \\ & \dot{k}(D_2) & & & \\ & & \cdot & & \\ & & & \cdot & \\ & & & & \dot{k}(D_n) \end{bmatrix} (\Delta\psi_o) + v_I(\psi_I) \tag{47}$$

which as before yields

$$(N_I) = [\dot{k}]\,(\Delta C_o) + v_I(C_I) \tag{48}$$

with

$$[\dot{k}] = [t] \begin{bmatrix} \dot{k}(D_1) & & & & \\ & \dot{k}(D_2) & & & \\ & & \cdot & & \\ & & & \cdot & \\ & & & & \dot{k}(D_n) \end{bmatrix} [t]^{-1} \tag{49}$$

Although $\dot{k}(D_i)$ depends upon v_I as well as D_i(1), this causes no difficulty because v_I is the same for all values of i. Hence

$$[\dot{k}] = \dot{k}([D]) \tag{50}$$

and Sylvester's theorem is used to carry out the expansion. It is not difficult to show that when it is used in place of $[k]$, $[\dot{k}]$ satisfies Equation (40) at high fluxes. Hence the expansion of Equation (50) by (the appropriate form of) Sylvester's theorem may be carried out whether or not $[D]$ can be diagonalized or k is analytic. The above results allow the prediction of the rates of mass transfer in multicomponent systems whenever the equivalent binary behavior is known. However the equivalent binary behavior is known only for constant physical properties, and since physical property variations tend to increase as the fluxes increase, the above results cannot be expected to apply when the fluxes are very large.

TRANSFER BETWEEN TWO PHASES

Consider transfer between two phases which may have different diffusion coefficient matrices. One wishes to obtain the multicomponent analogue of the overall binary mass transfer coefficient, the law of additivity of resistances. As in binary systems it is convenient to use equations of the form of (36) rather than (48) even when v_I cannot be neglected.

To simplify nomenclature Equation (36) is written with mole fractions rather than concentrations. Then if the component mole fractions in phase y are written as y_i, the rates of transfer to the interface from phase y are given by

$$(N_I) = [k_y]\,(\Delta y_o) = [k_y]\,\{(\bar{y}) - (y_I)\} \tag{51}$$

and the rates of transfer from the interface to phase x where the component mole fractions are x_i are given by

$$(N_I) = [k_x]\,\{(x_I) - (\bar{x})\} \tag{52}$$

and the two flux vectors are equal. If there is no interfacial resistance the mole fractions at the interface are related by the expression

$$(y_I) = [M]\,(x_I) \tag{53}$$

where $[M]$ is the $n \times n$ equilibrium constant matrix. Generalizing the usual expression for $y_i{}^*$, the mole fraction of component i which would be in equilibrium with $\bar{x}_i$, one gets

$$(y^*) = [M]\,(\bar{x}) \tag{54}$$

The interfacial mole fractions may be eliminated from the above equations to give

$$(N_I) = [K_y]\,\{(\bar{y}) - (y^*)\} = [K_y]\,(\Delta^o y) \tag{55}$$

where

$$[K_y]^{-1} = [k_y]^{-1} + [M]\,[k_x]^{-1} \tag{56}$$

so the individual mass transfer coefficient matrices combine in a manner analogous to the way the individual mass transfer coefficients combine in a binary system. The resulting overall mass transfer coefficient matrix $[K_y]$ plays the same role in multicomponent systems that the overall mass transfer coefficient plays in binary systems. If $(\Delta^o y)$ is considered to be the overall driving force, $[k_y]^{-1}$ is the resistance of phase y and $[M]\,[k_x]^{-1}$ is the resistance of phase x in the same units. Equation (56) then shows that the single-phase resistances are additive and their sum is the overall resistance $[K_y]^{-1}$. As in binary systems one phase controls only if the resistance of the other phase is negligible, but this condition is more stringent in multicomponent systems than in binary ones.

An overall mass transfer coefficient based on the x_i can also be obtained. Define as usual x_i^* as the concentration of component i which would be in equilibrium with $\bar{y}_i$. Then

$$(x^*) = [M]^{-1}\,(\bar{y}) \tag{57}$$

As before one then obtains

$$N_I = [K_x]\,\{(x^*) - (x)\} = [K_x]\,(\Delta^o x) \tag{58}$$

where

$$[K_x]^{-1} = [k_x]^{-1} + [M]^{-1}\,[k_y]^{-1} \tag{59}$$

and $[K_x]$ and $[K_y]$ are related by the expression

$$[K_x] = [K_y]\,[M] \tag{60}$$

If $(\Delta^o x)$ is taken to be the overall driving force, $[k_x]^{-1}$ is the resistance of phase x, $[M]^{-1}\,[k_y]^{-1}$ is the resistance of phase y, and these resistances sum to give the overall resistance $[K_x]^{-1}$.

As has been pointed out (6) when there is transfer between phases the boundary conditions on one phase may depend upon the behavior of the other phase, and strictly speaking Equation (1) must be solved simultaneously for both phases before $[k_y]$ and $[k_x]$ can be obtained. However practically speaking one may ignore this type of coupling and obtain $[k_y]$ and $[k_x]$ from the usual binary correlations of k_y and k_x which ignore this coupling, or from binary models which assume constant initial and boundary concentrations. Equation (55) or (58) may then be combined with material balances and the resulting equation integrated over the system.

The linearized method still depends upon the assumption of constant physical properties so it cannot be expected to quantitatively reproduce all the features of multicomponent mass transfer when concentration differences are large. Although a few limited tests were encouraging (6), the practical range of application of the linearized method is still to be determined.

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NOTATION

a, A = constants
b, B = boundaries b and B respectively
C_i = concentration of component i
(C) = column vector with elements C_i
D = diffusion coefficient
D_i = diffusion coefficient of combine i = roots of characteristic equation of D
D_{ij} = multicomponent diffusion coefficients
$[D]$ = multicomponent diffusion coefficient matrix
f = solution function
f_{ij} = elements of solution matrix $[f]$
$[f]$ = solution matrix
I = identity matrix
j_i = flux of component i with respect to reference velocity
(j) = column vector with elements j_i
k, k_i = binary mass transfer coefficients
$\dot{k}$ = Stewart binary mass transfer coefficient
k_{ij} = multicomponent mass transfer coefficients, elements of $[k]$
$[k]$ = multicomponent mass transfer coefficient matrix
$[\dot{k}]$ = multicomponent mass transfer coefficient matrix based on $\dot{k}$
$[k_y]$ = multicomponent mass transfer coefficient matrix for phase y based on mole fraction driving forces
$[k_x]$ = multicomponent mass transfer coefficient matrix for phase x based on mole fraction driving forces
$[K_y]$ = overall multicomponent mass transfer coefficient matrix based on $(\Delta^o y)$
$[K_x]$ = overall multicomponent mass transfer coefficient matrix based on $(\Delta^o x)$
$[M]$ = equilibrium constant matrix
n = number of components minus 1
N_i = flux of component i with respect to a fixed coordinate
(N) = column vector with elements N_i
r_i = rate of production of species i per unit volume by reaction
(r) = column vector with elements r_i
(R) = transformed form of (r)
S = distance normal to boundary
t_{ik} = elements of $[t]$
$[t]$ = modal matrix of $[D]$
T_{jk} = cofactor of element t_{kj} in $|t|$
V = reference velocity
v_I = normal component of reference velocity at interface
x_i = mole fraction of component in phase x
(x) = column vector whose elements are x_i
$(\Delta^o x)$ = overall driving force column vector based on x phase
y_i = mole fraction of component i in phase y
(y) = column vector whose elements are y_i
$(\Delta^o y)$ = overall driving force column vector based on y phase
$[Z_o]$ = matrix defined by Equation (24)
x, y, z = position coordinates

Greek Letters

δ_{ij} = Kronecker delta
Δ = difference
η_i = flux of combine i with respect to a fixed coordinate
(η) = column vector whose elements are η_i
θ = time
ψ_i = concentration of combine i
(ψ) = column vector whose elements are ψ_i
ϵ_i = flux of combine i with respect to the reference velocity
(ϵ) = column vector whose elements are ϵ_i

Subscripts

1, 2 . . . . . . n = components 1, 2, ... n
i, j, k, l = indices
I = interface
o = characteristic value
– = vector in x, y, x space

Superscripts

– = bulk average
* = equilibrium

Operators

∇' = gradient operator
$\nabla\cdot$ = divergence operator
∇^2 = Laplacian Operator
$|\ |$ = determinant

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