θ_{ad} = dimensionless adiabatic temperature defined by Equation (12*b*)

θ_{max} = maximum of θ reached at τ_{max}

θ_o = initial guess of θ needed for computational purposes

ν = frequency factor

ν_o = vibrational frequency at the interface of the new-old phase

ρ = density of the new phase

ρ' = density of the reacting mixture

σ = Stefan constant

τ = dimensionless time defined by Equation (5*a*)

τ_{max} = dimensionless time needed for completion of the reaction

LITERATURE CITED

Bowden, F. P., and O. A. Curton, "Birth and Growth of Explosion in Liquids and Solids Initiated by Impact and Friction," *Proc. Roy. Soc.*, **A198**, 350 (1949).

Bowden, F. P., and K. Singh, "Irradiation of Explosives with High-Speed Particles and the Influence of Crystal Size on Explosion," *ibid.*, **A227**, 22 (1954).

Bowden, F. P., and H. T. Williams, "Initiation and Propagation of Explosion in Azides and Fulminates," *ibid.*, **A208**, 176 (1951).

Bowden, F. P., and A. D. Yoffe, *Initiation and Growth of Explosion in Liquids and Solids*, Cambridge University Press, Cambridge, England (1952).

Bowden, F. P., and A. D. Yoffe, *Fast Reaction in Solids*, Butterworth, London, England (1958).

Chaudhri, M. M., and J. E. Field, "The Effect of Crystal Size on the Thermal Explosion of α-Lead Azide," *J. Solid State Chem.*, **12**, 72 (1975).

Frank-Kamenetskii, D. A., *Diffusion and Heat Transfer in Chemical Kinetics*, p. 374, Plenum Press, New York (1969).

Groocock, J. M., "The Thermal Explosion of α-Lead Azide," *Trans. Faraday Soc.*, **54**, 1526 (1958).

Jakob, M., *Heat Transfer*, Vol. I, p. 525, Wiley, New York (1949).

Ruckenstein, Eli, and T. Vavanellos, "Kinetics of Solid Phase Reactions," *AIChE J.*, **21**, 756 (1975).

Young, D. A., *Decomposition of Solids*, Pergamon Press, New York (1966).

Manuscript received October 2, 1975; revision received December 5 and accepted December 8, 1975.

A Multicomponent Film Model Incorporating a General Matrix Method of Solution to the Maxwell-Stefan Equations

RAJAMANI KRISHNA
and
G. L. STANDART

Department of Chemical Engineering
University of Manchester Institute of Science and Technology
Sackville Street
Manchester M60 1QD, England

Convenient expressions for calculating multicomponent gas phase mass transfer coefficients and transfer rates are obtained by use of an exact matrix method of solution to the Maxwell-Stefan equations. The results are seen to be exact matrix analogues of classical binary relations and may also be applied as an approximation to describe liquid phase transport.

SCOPE

Many chemical engineering operations such as distillation, absorption, condensation, and evaporation involve steady state transfer of three or more species, and it is important in such cases to calculate the rates of transfer in either phase. Often in practice one has to rely on some theory of mass transfer which in almost all cases is based on a model involving molecular diffusion. Although binary molecular diffusion theory is well understood, the interesting transfer characteristics of multicomponent systems—systems for which $n \geqq 3$—have only relatively recently been recognized and studied (Toor, 1957, 1964; Stewart and Prober, 1964). Thus, in multicomponent systems it is possible to obtain various interaction phenomena such as osmotic diffusion (transfer of a component in the absence of a composition gradient for that species), diffusion barrier (no transfer of a component even though a composition gradient exists for it), and reverse diffusion (diffusion of a species against its composition gradient). The correct description of multicomponent transport phenomena is obtained by using a matrix of mass transfer coefficients with nondiagonal coefficients. This work is concerned with the development of a film model for multicomponent mass transfer for calculating the matrix of transfer coefficients and is based on an exact matrix method of solution to the Maxwell-Stefan equations. The method developed in this work does not make the assumption of constant matrix of diffusion coefficients as required in the linearized theory development of Toor (1964) and Stewart and Prober (1964).

Correspondence concerning this paper should be addressed to R. Krishna.

CONCLUSIONS AND SIGNIFICANCE

The matrix of mass transfer coefficients under conditions of finite transfer rates is obtained as a product of two matrices: one, a matrix of zero flux mass transfer coefficients (which may be evaluated from binary transport data) and a correction factor matrix, which accounts for finite rates of transfer of the individual species. The expressions obtained are the exact matrix analogues of classical binary transfer rate relations at high rates of transfer (Bird, Stewart, and Lightfoot, 1960). The matrix formulation developed here is particularly convenient because the correction factor matrix has the proper limiting behavior (it reduces to the identity matrix for vanishing transfer rates), and the calculations of the transfer fluxes involve a simple and stable iteration procedure. The matrix method may be considered exact for mixtures of ideal gases; for dense gases and liquid mixtures, the analysis holds to a reasonable degree of approximation.

The results obtained in this work are directly applicable in the calculation of transfer rates for many separation processes and also for obtaining the external mass transfer resistances in heterogeneous reacting systems.

The rate relations for interphase mass transfer in n-component systems are properly formulated in terms of an $n - 1$ dimensional square matrix of (diffusive) mass transfer coefficients in either phase (Stewart and Prober, 1964; Toor, 1964). For the gas phase, for example, the diffusion fluxes are given by

$$(J^y) = [k^\bullet_y](y_b - y_I) \qquad (1)$$

where $(y_b - y_I)$ represents an $n - 1$ dimensional column matrix of composition driving forces. In many practical chemical engineering operations, the compositions in the bulk phase are known and remain constant at a given position in the equipment for steady state conditions. The compositions at the interface are either known or can be eliminated by use of overall driving forces and mass transfer coefficients. For discussions in this paper, we shall assume that the interface compositions are specified. The superscript • on the matrix of mass transfer coefficients $[k^\bullet_y]$ serves as a reminder that these coefficients are themselves dependent on the interfacial rates of transfer of the n species N_i (Stewart, 1973).

Only $n - 1$ of the diffusion fluxes J_i^y are independent, for we have the requirement

$$\sum_{i=1}^{n} J_i^y = 0 \qquad (2)$$

The phase invariant total fluxes N_i are calculated from

$$N_i = J_i^y + y_i N_t \quad i = 1, 2, \ldots n \qquad (3)$$

with an additional determinancy condition (Standart et al., 1974). For transport within a liquid phase, we have expressions analogous to equations (1) to (3) above.

The calculation of the diffusion fluxes J_i requires the knowledge of the $(n - 1)^2$ elements of the matrix $[k^\bullet]$. The linearized theory of multicomponent mass transfer, pioneered by Toor (1964) and Stewart and Prober (1964), may be used to obtain the multicomponent transfer coefficients from information on binary transport parameters. The linearized theory relies for its development on the assumption that the matrix of diffusion coefficients $[D]$ remains constant along the direction of transfer; this assumption has been shown to be adequate for many cases (Arnold and Toor, 1967; Johns and DeGance, 1975).

It is the purpose of this paper to develop an exact film model for multicomponent gas phase mass transport without making the assumption of constant matrix of diffusion coefficients. The development is based on an exact matrix method of solution to the Maxwell-Stefan equations. The limitations of the linearized theory of multicomponent mass transfer are explored. The problems associated with estimating the matrix $[k^\bullet_x]$ for liquid mixtures are discussed, and some improved approximate procedures are suggested.

MULTICOMPONENT FILM MODEL FOR GAS PHASE MASS TRANSPORT

Consider mass transfer in an ideal gas mixture, consisting of n species, at constant temperature and pressure (with suitably averaged properties, the analysis below will hold for nonisothermal conditions as well). The total molar density of the gas mixture is therefore constant and given by

$$c = p/RT \qquad (4)$$

The composition of the gaseous mixture in the bulk gas core is assumed to remain constant at the values y_{ib}, while the interface compositions are similarly held constant at y_{iI}. The transition between the bulk vapor compositions to the interface vapor compositions is assumed to take place through a thin film of thickness δ by molecular transport mechanism.

The correct description of molecular diffusion in an n-component system under isothermal-isobaric conditions is given by the Maxwell-Stefan equations, which for steady state unidirectional transfer reduce to

$$\frac{dy_i}{dz} = \sum_{\substack{k=1\\k\neq i}}^{n} \frac{y_i N_k - y_k N_i}{c\mathcal{D}_{ik}} \quad i = 1, 2, \ldots n - 1 \qquad (5)$$

Only $n - 1$ Equations (5) are written, for we have composition gradient for the n^{th} species determined by

$$\frac{dy_n}{dz} = -\sum_{i=1}^{n-1} \frac{dy_i}{dz} \qquad (6)$$

The representation (5) is particularly convenient because the coefficients $\mathcal{D}_{ik}$, which represent the diffusivities of the binary pairs $i - k$ in the mixture, are virtually composition independent for ideal gas mixtures; these coefficients can be calculated to a high degree of accuracy from the molecular parameters of the Chapman-Enskog kinetic theory (see, for example, Chapman and Cowling, 1970). Analytic solutions to (5) are available for ternary gas mixtures in special cases (Gilliland, 1937; Toor, 1957; Hsu and Bird, 1960; Johns and DeGance, 1975). Here we seek a convenient general solution to the n-component case.

It is convenient to define a dimensionless distance coordinate in the film η as

$$\eta = z/\delta \qquad (7)$$

and the coefficients

$$\mathcal{K}_{ik} = c\mathcal{D}_{ik}/\delta \qquad \begin{matrix} i,k = 1, 2, \ldots n \\ i \neq k \end{matrix} \qquad (8)$$

These coefficients $\mathcal{K}_{ik}$ are the binary mass transfer coefficients of the pairs $i - k$ in the n-component mixture, corresponding to zero-flux conditions (Bird, Stewart, and Lightfoot, 1960).

With definitions (7) and (8) above, the Equations (5) may be rewritten as

$$\frac{dy_i}{d\eta} = \sum_{\substack{k=1 \\ k \neq i}}^{n} \frac{y_i N_k - y_k N_i}{\mathcal{K}_{ik}} \qquad i = 1, 2, \ldots n - 1 \qquad (9)$$

or, in terms of the diffusion fluxes J_i^y, as [see Equation (3)]

$$\frac{dy_i}{d\eta} = \sum_{\substack{k=1 \\ k \neq i}}^{n} \frac{y_i J_k^y - y_k J_i^y}{\mathcal{K}_{ik}} \qquad i = 1, 2, \ldots n - 1 \qquad (10)$$

The diffusion fluxes J_i^y of course change in value across the film, while the total fluxes N_i are phase invariant. We shall return to Equations (10) at a later stage; here we develop the integrations of Equations (9).

It is convenient to write Equations (9) in $n - 1$ dimensional matrix notation as

$$\frac{d(y)}{d\eta} = [\Phi](y) + (\zeta) \qquad (11)$$

where the elements of the square matrix $[\Phi]$ are given by

$$\Phi_{ii} = \frac{N_i}{\mathcal{K}_{in}} + \sum_{\substack{k=1 \\ k \neq i}}^{n} \frac{N_k}{\mathcal{K}_{ik}} \qquad i = 1, 2, \ldots n - 1 \qquad (12)$$

$$\Phi_{ij} = -N_i \alpha_{ij} \qquad \begin{matrix} i,j = 1, 2, \ldots n - 1 \\ i \neq j \end{matrix} \qquad (13)$$

with the α_{ij} defined as

$$\alpha_{ij} \equiv 1/\mathcal{K}_{ij} - 1/\mathcal{K}_{in} \qquad \begin{matrix} i,j = 1, 2, \ldots n - 1 \\ i \neq j \end{matrix} \qquad (14)$$

The elements of the column matrix (ζ) are given by

$$\zeta_i = -N_i/\mathcal{K}_{in} \qquad i = 1, 2, \ldots n - 1 \qquad (15)$$

The total molar fluxes N_i and the coefficients $\mathcal{K}_{ik}$ are independent of the position η within the film, and therefore the linear matrix differential Equation (11) can be solved with the condition

$$\text{at } z = 0, \quad \eta = 0, \quad (\text{bulk gas}), \quad (y) = (y_b) \qquad (16)$$

to give the composition profile within the film as (Amundson, 1966)

$$(y_\eta - y_b) = \{\exp[\Phi]\eta - \ulcorner I \lrcorner\}\{(y_b) + [\Phi]^{-1}(\zeta)\} \qquad (17)$$

Substituting the condition

$$\text{at } z = \delta, \quad \eta = 1, \quad (\text{interface}), \quad (y) = (y_I) \qquad (18)$$

in Equation (17), we get

$$(y_I - y_b) = \{\exp[\Phi] - \ulcorner I \lrcorner\}\{(y_b) + [\Phi]^{-1}(\zeta)\} \qquad (19)$$

A combination of Equations (17) and (19) gives the composition profiles within the film in terms of the total fluxes and the compositions at either end of the diffusion path as

$$(y_\eta - y_b) = \{\exp[\Phi]\eta - \ulcorner I \lrcorner\}\{\exp[\Phi] - \ulcorner I \lrcorner\}^{-1}(y_I - y_b) \qquad (20)$$

which is the exact matrix analogue of the well-known composition profile for a binary system (Bird, Stewart, and Lightfoot, 1960)

$$\frac{y_1 - y_{1b}}{y_{1I} - y_{1b}} = \frac{\exp\phi\eta - 1}{\exp\phi - 1} \qquad (21)$$

with the dimensionless rate factor Φ given as

$$\phi = (N_1 + N_2)/\mathcal{K}_{12} \qquad (22)$$

Now, for binary systems the diffusion flux for component 1 in the bulk gas is given by

$$J_{1b}^y = -\mathcal{K}_{12} \left.\frac{dy_1}{d\eta}\right|_{\eta=0} \qquad (23)$$

and we obtain in view of Equation (21)

$$J_{1b}^y = \mathcal{K}_{12} \frac{\phi}{\exp\phi - 1} (y_{1b} - y_{1I}) \qquad (24)$$

It is convenient to define the finite flux binary mass transfer coefficient in the bulk gas phase by

$$J_{1b}^y = \mathcal{K}^{\bullet}_{b12}(y_{1b} - y_{1I}) \qquad (25)$$

which gives the film theory estimation of these finite flux coefficients as [see Equations (24) and (25)]

$$\mathcal{K}^{\bullet}_{b12} = \mathcal{K}_{12} \frac{\phi}{\exp\phi - 1} \qquad (26)$$

In proceeding with the matrix analysis of multicomponent mass transport rate relations, we shall seek proper matrix generalizations of the binary relationships (23) to (26).

The first step is to define a matrix of zero flux mass transfer coefficients in the bulk gas phase $[k_{yb}]$ by

$$(J_b^y) = -[k_{yb}] \left.\frac{d(y)}{d\eta}\right|_{\eta=0} \qquad (27)$$

In order to calculate $[k_{yb}]$, we observe that the Equations (10) can be written in matrix notation as

$$\frac{d(y)}{d\eta} = -[\mathcal{B}](J^y) \qquad (28)$$

where the elements of the square matrix $[\mathcal{B}]$ (equivalent to the Stewart and Prober matrix $[A]$) are obtained as

$$\mathcal{B}_{ii} = \frac{y_i}{\mathcal{K}_{in}} + \sum_{\substack{k=1 \\ k \neq i}}^{n} \frac{y_k}{\mathcal{K}_{ik}} \qquad i = 1, 2, \ldots n - 1 \qquad (29)$$

$$\mathcal{B}_{ij} = -y_i \alpha_{ij} \qquad \begin{matrix} i,j = 1, 2, \ldots n - 1 \\ i \neq j \end{matrix} \qquad (30)$$

The composition gradient in the bulk gas phase $\eta = 0$ is obtained from Equation (28) as

$$\left.\frac{d(y)}{d\eta}\right|_{\eta=0} = -[\mathcal{B}_b](J_b^y) \qquad (31)$$

where the matrix $[\mathcal{B}_b]$ is evaluated from Equation (29) and (30) with all compositions y_i taken as y_{ib}, the bulk gas phase values.

Comparison of Equations (27) and (31) shows that the matrix of zero flux mass transfer coefficients in the bulk gas phase $[k_{yb}]$ is just the inverse of the matrix $[\mathcal{B}_b]$; that is

$$[k_{yb}] = [\mathcal{B}_b]^{-1} \tag{32}$$

The matrix inversion can be carried out explicitly for a ternary system, and the results are

$$k_{yb11} = \mathcal{K}_{13}(y_{1b}\mathcal{K}_{23} + (1 - y_{1b})\mathcal{K}_{12})/S \tag{33}$$

$$k_{yb12} = y_{1b}\mathcal{K}_{23}(\mathcal{K}_{13} - \mathcal{K}_{12})/S \tag{34}$$

$$k_{yb21} = y_{2b}\mathcal{K}_{13}(\mathcal{K}_{23} - \mathcal{K}_{12})/S \tag{35}$$

$$k_{yb22} = \mathcal{K}_{23}(y_{2b}\mathcal{K}_{13} + (1 - y_{2b})\mathcal{K}_{12})/S \tag{36}$$

where

$$S = y_{1b}\mathcal{K}_{23} + y_{2b}\mathcal{K}_{13} + y_{3b}\mathcal{K}_{12} \tag{37}$$

The composition gradient in the bulk gas phase can be obtained from the composition profile (20) as

$$\left.\frac{d(y)}{d\eta}\right|_{\eta=0} = -[\Phi]\{\exp[\Phi] - \lceil I \rfloor\}^{-1}(y_b - y_I) \tag{38}$$

A combination of Equations (27) and (38) gives

$$(J_b^y) = [k_{yb}][\Phi]\{\exp[\Phi] - \lceil I \rfloor\}^{-1}(y_b - y_I) \tag{39}$$

which is the matrix generalization of the binary rate relation (24). The matrix of finite flux mass transfer coefficients $[k^{\bullet}_{yb}]$ is obtained by comparison of Equations (1) and (39) as

$$[k^{\bullet}_{yb}] = [k_{yb}][\Phi]\{\exp[\Phi] - \lceil I \rfloor\}^{-1} \tag{40}$$

which is the matrix analogue of Equation (26) and is the result we sought; it allows calculation of the finite flux coefficients from information on zero flux binary mass transfer coefficients and the rates of transfer N_i. The determination of the diffusion fluxes J_{ib}^y and the total fluxes N_i is not explicit in the true sense because a prior knowledge of the molar fluxes is required in the calculation of $[k^{\bullet}_{yb}]$. We shall, in fact, observe that the formulation (40) is a very convenient one.

In proceeding with the discussions, it becomes convenient to define a correction factor matrix

$$[\Xi] \equiv [\Phi]\{\exp[\Phi] - \lceil I \rfloor\}^{-1} \tag{41}$$

Consider the limiting case in which all the total fluxes N_i tend to vanish; the matrix $[\Phi]$ tends to the null matrix $[0]$; that is

$$\lim_{\substack{i = 1, 2, \ldots n \\ N_i \to 0}} [\Phi] = [0] \tag{42}$$

and the correction factor matrix tends to the identity matrix $\lceil I \rfloor$; that is

$$\lim_{\substack{Ni \to 0, \\ i = 1, 2, \ldots n}} [\Xi] = \lceil I \rfloor \tag{43}$$

and therefore

$$\lim_{\substack{N_i \to 0, \\ i = 1, 2, \ldots n}} [k^{\bullet}_{yb}] = [k_{yb}] \tag{44}$$

For finite but low rates of mass transfer, the relation (44) provides a good estimate of the transfer coefficient matrix $[k^{\bullet}_{yb}]$; this, in fact, suggests a stable iteration procedure for calculating the total fluxes for fixed two-point boundary value problems.

1. Estimate the zero flux binary mass transfer coefficients $\mathcal{K}_{ik}$ from the binary diffusivity in the gas phase $\mathcal{D}_{ik}$ by using the knowledge of the film thickness or from an appropriate mass transfer correlation, say of the j factor type.

2. Calculate the matrix of zero flux mass transfer coefficients at the bulk gas phase conditions, $[k_{yb}]$, from relation (32).

3. Assume the correction factor matrix $[\Xi]$ to be the identity matrix and hence use relation (44).

4. With this estimate of the matrix $[k^{\bullet}_{yb}]$, calculate the diffusion fluxes J_{ib}^y from Equation (1). The total fluxes N_i are obtained from Equations (3) with an additional determinancy condition.

5. This estimate of the fluxes N_i allows calculation of the elements of $[\Phi]$ and therefore of the correction factor matrix $[\Xi]$ from Equation (41). The correction factor matrix $[\Xi]$ is most simply evaluated by use of Sylvester's expansion theorem, details of which can be found in, for example, Amundson (1966).

6. A new estimate of $[k^{\bullet}_{yb}]$ is obtained from the relation

$$[k^{\bullet}_{yb}] = [k_{yb}][\Xi] \tag{45}$$

and steps 4 to 6 are repeated till convergence is obtained for each individual flux N_i.

SPECIAL CASES

For a ternary mixture, the correction factor matrix $[\Xi]$ can be evaluated explicitly by using Sylvester's theorem; the result is

$$\Xi_{11} = \frac{\hat{\Xi}_1(\Phi_{11} - \hat{\Phi}_2) - \hat{\Xi}_2(\Phi_{11} - \hat{\Phi}_1)}{(\hat{\Phi}_1 - \hat{\Phi}_2)} \tag{46}$$

$$\Xi_{12} = \frac{(\hat{\Xi}_1 - \hat{\Xi}_2)}{(\hat{\Phi}_1 - \hat{\Phi}_2)}\Phi_{12} \tag{47}$$

$$\Xi_{21} = \frac{(\hat{\Xi}_1 - \hat{\Xi}_2)}{(\hat{\Phi}_1 - \hat{\Phi}_2)}\Phi_{21} \tag{48}$$

$$\Xi_{22} = \frac{\hat{\Xi}_1(\Phi_{22} - \hat{\Phi}_2) - \hat{\Xi}_2(\Phi_{22} - \hat{\Phi}_1)}{(\hat{\Phi}_1 - \hat{\Phi}_2)} \tag{49}$$

where $\hat{\Phi}_1$ and $\hat{\Phi}_2$ are the eigenvalues of the matrix $[\Phi]$, and $\hat{\Xi}_1$ and $\hat{\Xi}_2$ are defined as

$$\hat{\Xi}_i = \frac{\hat{\Phi}_i}{\exp\hat{\Phi}_i - 1} \quad i = 1, 2 \tag{50}$$

For the special case of equimolar counter transfer in a ternary mixture

$$N_t = N_1 + N_2 + N_3 = 0 \tag{51}$$

the eigenvalues $\hat{\Phi}_i$ are determined as

$$\hat{\Phi}_1 = N_1\alpha_{21} + N_2\alpha_{12} \tag{52}$$

and

$$\hat{\Phi}_2 = 0 \tag{53}$$

The elements of the correction factor matrix for this case are obtained as

$$\Xi_{11} = (\hat{\Xi}_1\Phi_{11} + \Phi_{22})/\hat{\Phi}_1 \tag{54}$$

$$\Xi_{12} = (\hat{\Xi}_1 - 1)\Phi_{12}/\hat{\Phi}_1 \tag{55}$$

$$\Xi_{21} = (\hat{\Xi}_1 - 1)\Phi_{21}/\hat{\Phi}_1 \tag{56}$$

$$\Xi_{22} = (\hat{\Xi}_1\Phi_{22} + \Phi_{11})/\hat{\Phi}_1 \tag{57}$$

For transfer of two species through a third stagnant component

$$N_3 = 0 \tag{58}$$

and for this special case the eigenvalues of the matrix $[\Phi]$ are obtained as

$$\hat{\Phi}_1 = N_1/K_{13} + N_2/K_{23} \tag{59}$$

and

$$\hat{\Phi}_2 = (N_1 + N_2)/K_{12} \tag{60}$$

The Equations (46) to (49) simplify to

$$\Xi_{11} = (\hat{\Xi}_1\Phi_{12} + \hat{\Xi}_2\Phi_{21})/(\hat{\Phi}_1 - \hat{\Phi}_2) \tag{61}$$

$$\Xi_{12} = (\hat{\Xi}_1 - \hat{\Xi}_2)\Phi_{12}/(\hat{\Phi}_1 - \hat{\Phi}_2) \tag{62}$$

$$\Xi_{21} = (\hat{\Xi}_1 - \hat{\Xi}_2)\Phi_{21}/(\hat{\Phi}_1 - \hat{\Phi}_2) \tag{63}$$

$$\Xi_{22} = (\hat{\Xi}_1\Phi_{21} + \hat{\Xi}_2\Phi_{12})/(\hat{\Phi}_1 - \hat{\Phi}_2) \tag{64}$$

For the special determinancy conditions (51) and (58), analytic solutions in parametric form are available in the literature (Gilliland, 1937; Toor, 1957). These solutions, however, suffer from a major drawback that multiple roots are possible (Sherwood, 1937; Toor, 1957). The matrix method presented here is very stable, and convergence is obtained in a small number of iterations for a variety of problems tested (Krishna, 1975). The stability of the matrix method of solution presented here is due to the fact that all peculiarities of multicomponent transport phenomena are essentially lumped into the form of the correction factor matrix $[\Xi]$ which has the proper limiting behavior. Further, the Gilliland and Toor solutions involve taking the logarithm of a quotient; it is possible for either term in the numerator or denominator to vanish or assume negative values during the course of an iteration procedure. These solutions will therefore fail under these circumstances. The matrix method does not have this drawback.

where $[P]$ is the modal matrix of $[D]$. The pseudo finite flux mass transfer coefficients are related to the pseudo zero flux mass transfer coeffiicents by

$$\check{k}^\bullet_{yi} = \check{k}_{yi}\frac{\check{\phi}_i}{\exp\check{\phi}_i - 1} \quad i = 1, 2, \ldots n - 1 \tag{66}$$

where

$$\check{\phi}_i = N_t/\check{k}_{yi} \quad i = 1, 2, \ldots n - 1 \tag{67}$$

and

$$\check{k}_{yi} = c\check{D}_i/\delta \quad i = 1, 2, \ldots n - 1 \tag{68}$$

From Equations (66) and (67) we note that it is only the net total mixture flux N_t and not the individual species fluxes N_i which appear in the flux corrections. The vanishing of the total mixture flux ($N_t \rightarrow 0$) is sufficient to give a unity correction factor [see Equations (66) and (67)]. By contrast, the exact matrix analysis presented here shows that each individual total flux N_i will offer its own intrinsic contribution to the correction factor matrix $[\Xi]$, which reduces to the identity matrix when every individual flux vanishes [see Equations (54) to (57) for the equimolar counter transfer case]. We might expect the linearized theory to be in error when the transferring species have widely different rates of transfer in addition to having widely different mobilities. This is found to be the case as shown in the example below.

Consider steady state transfer of acetone (1) and benzene (2) through stagnant helium (3) with the following boundary conditions:

$$\begin{aligned} &\text{at} \quad \eta = 0, \quad y_{1b} = 0.10; \quad y_{2b} = 0.00 \\ &\text{at} \quad \eta = 1, \quad y_{1I} = 0.02; \quad y_{2I} = 0.28 \end{aligned} \tag{69}$$

The diffusivities of the binary pairs are estimated to be

$$\mathcal{D}_{12} = 4\ \text{mm}^2/\text{s}; \quad \mathcal{D}_{13} = 41\ \text{mm}^2/\text{s}; \quad \mathcal{D}_{23} = 39\ \text{mm}^2/\text{s}$$

The calculation of the finite flux mass transfer coefficients and transfer rates by the matrix method and the linearized theory method are summarized below:

	N_1 c/δ mm^2/s	N_2 c/δ mm^2/s	$k^\bullet_{yb11}$ c/δ mm^2/s	$k^\bullet_{yb12}$ c/δ mm^2/s	$k^\bullet_{yb21}$ c/δ mm^2/s	$k^\bullet_{yb22}$ c/δ mm^2/s
Exact matrix method	−0.39	−9.43	78.85	20.41	−31.05	24.81
Linearized theory ($[k_y^\bullet]$ calculated at average composition)	−0.90	−8.95	27.54	7.57	17.56	36.98

COMPARISON OF MATRIX METHOD WITH LINEARIZED THEORY APPROACH

It is interesting to compare our exact matrix method of solving the Maxwell-Stefan equations with the linearized theory approach of Stewart and Prober (1964) and Toor (1964). Basically, in the linearized theory approach one assumes that the matrix of diffusion coefficients $[D]$ stays constant across the film; this linearization and subsequent diagonalization of the coupled diffusion equations allows solution of the differential equations in terms of pseudo compositions and eigenvalues of the diffusion coefficient matrix. The solution in terms of the original variables is recovered by applying the reverse transformation. The matrix of finite flux mass transfer coefficients is obtained as (Stewart, 1973)

$$[k^\bullet_y] = [P]\ulcorner\check{k}^\bullet_y\lrcorner[P]^{-1} \tag{65}$$

The assumption of constant matrix of diffusion coefficient matrix of diffusion coefficients is clearly inadequate for the above example, and the molar flux of acetone calculated by the linearized method is subject to a large error.

MULTICOMPONENT MASS TRANSPORT IN LIQUID MIXTURES

For nonideal liquid mixtures, the correct description of the diffusion process is given by the generalized Maxwell-Stefan equations. For unidirectional diffusion in an n-component mixture at constant temperature, these equations take the form analogous to Equations (9) as

$$x_i\frac{d\ln\gamma_i x_i}{d\eta} = \sum_{\substack{k=1\\k\neq i}}^{n}\frac{x_iN_k - x_kN_i}{K_{xik}} \quad i = 1, 2, \ldots n - 1$$

where γ_i is the activity coefficient in solution, and the coefficients K_{xik} are defined by

$$K_{xik} = c\text{Đ}_{ik}/\delta \qquad \begin{matrix} i, k = 1, 2, \ldots n \\ i \neq k \end{matrix} \tag{71}$$

where the coefficients Đ_{ik} are the generalized Maxwell-Stefan diffusion coefficients. For ideal gas mixtures, we have, of course, $\gamma_i = 1$ and

$$\text{Đ}_{ik} = \mathcal{D}_{ik} \qquad \begin{matrix} i, k = 1, 2, \ldots. n \\ i \neq k \end{matrix} \tag{72}$$

Unlike the gas phase diffusion coefficients, the generalized Maxwell-Stefan diffusion coefficients are functions of composition in addition to being functions of temperature and pressure. Further, the Đ_{ik} are parameters describing the $i - k$ pair interactions, essentially kinetic, in the multicomponent mixture; they cannot therefore be identified with the binary liquid phase diffusion coefficient $\mathcal{D}_{xik}$. If we assume that the K_{xik} and γ_i are essentially constant over the diffusion path, then Equations (70) essentially reduce to Equations (9) and may therefore be solved by using the matrix method developed in this work. The above assumptions are better approximaions than the assumption of a constant matrix of diffusion coeffiicents in the liquid phase $[D_x]$ made by the linearized theory development of Stewart and Prober (1964) and Toor (1964).

CONCLUSIONS

A general matrix method for solving the Maxwell-Stefan equations describing isothermal-isobaric diffusion in multicomponent ideal gas mixtures has been developed. The resulting expressions for the diffusion fluxes and matrix of transfer coefficients are exact matrix analogues of classical binary relations. The advantages of the matrix method over published analytic solutions for special cases (Gilliland, 1937; Hsu and Bird, 1960; Toor, 1957; Johns and DeGance, 1975) are as follows.

1. The matrix method is applicable to the general n-component case, while published analyses are essentially restricted to ternary systems.
2. The formulation of the solution in terms of matrix of finite flux mass transfer coefficients, which is further expressed in terms of a product of a zero flux transfer coefficient matrix and a correction factor matrix, is particularly convenient because it affords a simple film theory estimation of the multicomponent transport coefficients.
3. The matrix method is stable and does not have the drawbacks of the Gilliland and Toor solutions, which give rise to multiple roots in some cases.

The matrix method is simple to use and must be considered preferable to the linearized theory method for the general case.

NOTATION

$[\mathcal{B}]$ = inverted matrix of multicomponent mass transfer coefficients, [kmole/(s)(m^2)(mole fraction)]$^{-1}$, elements of which are defined by Equations (29) and (30)
c = molar density of fluid mixture, kmole/m^3
$[D]$ = matrix of diffusion coefficients, m^2/s
Đ_{ik} = generalized Maxwell-Stefan diffusion coefficient for pair $i - k$ in multicomponent mixture, m^2/s
$\mathcal{D}_{ik}$ = diffusion coefficient of binary pair $i - k$, m^2/s
$\check{D}_i$ = characteristic roots (eigenvalues) of $[D]$, m^2/s
${}^{\ulcorner}I_{\lrcorner}$ = identity matrix with elements δ_{ik}
J_i = molar diffusion flux of species i, kmole/(s)(m^2)
$[k]$ = matrix of zero flux multicomponent mass transfer coefficients, kmole/(s)(m^2)(mole fraction)
$[k^\bullet]$ = matrix of finite flux multicomponent mass transfer coefficients, kmole/(s)(m^2)(mole fraction)
$\check{k}_i$ = eigenvalues of matrix $[k]$, kmole/(s)(m^2)(mole fraction)
$\check{k}^\bullet_i$ = eigenvalues of matrix $[k^\bullet]$, kmole/(s)(m^2)(mole fraction)
K_{12} = zero flux mass transfer coefficient in binary mixture of 1 and 2, kmole/(s)(m^2)(mole fraction)
K_{ik} = zero flux mass transfer coefficient of pair $i - k$ in multicomponent mixture, kmole/(s)(m^2)(mole fraction)
n = number of species in mixture
N_i = total molar flux of species i, kmole/(s)(m^2)
N_t = total mixture molar flux, kmole/(s)(m^2)
p = total system pressure, N/m^2
$[P]$ = modal matrix of $[D]$
R = gas constant, 8 314 J/(kmole)(K)
T = absolute temperature, K
x_i = mole fraction of species i in the liquid mixture
y_i = mole fraction of species i in the gas mixture
z = position along film, m

Greek Letters

α_{ij} = parameters defined by Equations (14), [kmole/(s)(m^2)(mole fraction)]$^{-1}$
γ_i = activity coefficient of species i in solution
δ = film thickness, m
δ_{ik} = Kronecker delta
(ζ) = column matrix with elements given by Equations (15)
η = dimensionless distance within the film
$[\Xi]$ = matrix of correction factors
ϕ = dimensionless rate factor for binary system, defined by Equation (22)
$\check{\phi}_i$ = dimensionless rate factor for pseudo species i, defined by Equation (67)
$[\Phi]$ = matrix of dimensionless rate factors for multicomponent system, with elements given by Equations (12) and (13)

Matrix Notation

$(\ )$ = column matrix of dimension $n - 1$
$[\ ]$ = square matrix, $(n - 1) \times (n - 1)$
$[\ ]^{-1}$ = inverted matrix
${}^{\ulcorner}\ {}_{\lrcorner}$ = diagonal matrix

Subscripts

b = bulk phase property
i, j, k = indexes
I = interfacial property
x = liquid phase
y = vapor phase
t = pertaining to total mixture

Superscripts

$\vee$ = pseudo property
$\wedge$ = eigenvalue of corresponding matrix
x = liquid phase property
y = vapor phase property
$\bullet$ = coefficients corresponding to finite transfer rates

LITERATURE CITED

Amundson, N. R., *Mathematical Methods in Chemical Engineering*, Prentice Hall, Englewood Cliffs, N. J. (1966).

Arnold, K. R., and H. L. Toor, "Unsteady Diffusion in Ternary Gas Mixture," *AIChE J.*, **13**, 909 (1967).

Bird, R. B., W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, Wiley, New York (1960).
Chapman, S., and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases*, 3 ed., prepared in co-operation with D. Burnett, Cambridge University Press, England (1970).
Gilliland, E. R., in *Absorption and Extraction*, T. K. Sherwood, 1 ed., McGraw Hill, New York (1937).
Hsu, H-W., and R. B. Bird, "Multicomponent Diffusion Problems," *AIChE J.*, **6**, 516 (1960).
Johns, L. E., and A. E. DeGance, "Diffusion in Ternary Ideal Gas Mixtures. I. On the Solution of the Stefan-Maxwell Equation for Steady Diffusion in Thin Films," *Ind. Eng. Chem. Fundamentals*, **14**, 237 (1975).
Krishna, R., "Interphase Transport of Mass and Energy in Multicomponent Systems," Ph.D. thesis, Department of Chemical Engineering, University of Manchester Institute of Science and Technology, Manchester, England (1975).
Standart, G. L., R. Krishna, and H. T. Cullinan, "Multicomponent Isothermal Mass Transfer," Paper presented at the AIChE Conference, Tulsa, Okla. (Mar., 1974).
Stewart, W. E., and R. Prober, "Matrix Calculation of Multicomponent Mass Transfer in Isothermal Systems," *Ind. Eng. Chem. Fundamentals*, **3**, 224 (1964).
Stewart, W. E., "Multicomponent Mass Transfer in Turbulent Flow," *AIChE J.*, **19**, 398 (1973).
Toor, H. L., "Diffusion in Three-component Gas Mixtures," *ibid.*, **3**, 198 (1957).
———, "Solutions of the Linearized Equations of Multicomponent Mass Transfer. II. Matrix Methods," *ibid.*, **10**, 460 (1964).

Manuscript received October 21, 1975; revision received December 9, and accepted December 11, 1975.

Evaluation of a Rapid Technique for Measuring the Diffusion Coefficients of Small Molecules

MARC LEMAGUER
F. H. WOLFE
and
T. G. SMYRL

Department of Food Science
University of Alberta
Edmonton, Alberta, Canada

The diffusion coefficients of sucrose, glycol, and glycine in water have been measured at 25.0°C by using the schlieren optical system of a preparative ultracentrifuge. The schlieren optical system was modified by the incorporation of a 35 mm single lens reflex camera. The values obtained were well within 2% of values found in existing literature and had an intrinsic precision of better than 2%.

SCOPE

The measurement of diffusion coefficients of small molecules has traditionally been restricted to well-known classical techniques such as those employing the Tiselius cell in conjunction with interference optics or those using the Stokes type of diaphragm cell. Although the reliability of these techniques is well established, they tend to require substantial amounts of time to obtain a diffusion measurement (Holmes, 1960; English and Dole, 1950).

For many years the ultracentrifuge with schlieren, absorption, or interference optical systems has been used in diffusion and sedimentation studies of macromolecular species in aqueous solution. Recently, however, Chandrasekhar and Hoelscher (1975) have extended the use of an analytical ultracentrifuge to the measurement of the diffusion coefficients of glycerol, glycol, and *n*-butanol in aqueous solution. Independently of Chandrasekhar and Hoelscher (1975), we have been studying the applicability of the ultracentrifugal technique to the measurement of diffusion coefficients of low molecular weight compounds using a preparative ultracentrifuge of which the schlieren optical attachment has been adapted to 35 mm photography. By using a double sector capillary synthetic boundary cell as the diffusion cell, the diffusion coefficients of sucrose, glycol, and glycine in water have been determined, and the results are compared to those obtained from interferometric techniques. In view of the fact that such preparative ultracentrifuges are commonly used, the rapid, simple, and accurate determination of diffusion coefficients of low molecular weight compounds is thus made available to a greater number of investigators.

CONCLUSIONS AND SIGNIFICANCE

A preparative ultracentrifuge equipped with a schlieren optical system has been used to obtain diffusion coefficients of sucrose, glycol, and glycine in water. The schlieren optical column has been modified so that a 35 mm single lens reflex camera can be used to record the schlieren patterns. With this apparatus, the diffusion coefficients were found to vary by less than 2% from values obtained by interference techniques. Replicate

---

Correspondence concerning this paper should be addressed to Marc LeMaguer.