Solution of the Linearized Equations of Multicomponent Mass Transfer: I

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The linearized equations of diffusion in a multicomponent system with flow and chemical reaction are shown to reduce to a set of equivalent binary diffusion equations.

The concentrations and fluxes in a multicomponent system are described by linear combinations of appropriate solutions to the binary diffusion equation for steady and unsteady diffusion and convective mass transfer, laminar or turbulent.

The rate of transfer of each component in a nonreacting *n* component system is a linear combination of the *n*-1 independent driving forces with proportionality constants which depend upon the multicomponent diffusion coefficients and appropriate binary mass transfer coefficients, while the concentration profile of each component is a linear combination of appropriate binary concentration profiles with proportionality constants which depend upon the multicomponent diffusion coefficients and the characteristic displacement from equilibrium of each component.

***The linearized theory is exact for small changes in concentration* but needs further testing when the concentration changes and fluxes are large.**

Solutions of the equations of mass transfer in multicomponent systems whether exact or approximate are available only for some special situations (*2, 3, 5, 12, 14, 17, 19, 20, 21, 29, 30, 31, 32*). The effective diffusivity methods of solution (*2, 18, 19, 20, 25, 28, 36*) are also limited either to steady state diffusion through a film, or to special situations in which the active component behaves as if it were in a binary mixture. Thus at present the essential nature of multicomponent mass transfer is either in the main uncertain (as in transient processes) or can be deduced only by using rather limited, simplified, models (as in convective mass transfer).

In this paper the general mass transfer behavior of multicomponent systems is obtained by reducing the linearized multicomponent mass transfer equations to a set of equivalent binary equations.

The continuity equation for each of the $n - 1$ independent components in an n component mixture is

$$\frac{\partial C_i}{\partial \theta} + \nabla \cdot \underline{N_i} = r_i, \quad i = 1, .., n-1 \tag{1}$$

and the general relationship between the fluxes and concentration gradients for isothermal, isobaric multicomponent systems in the absence of external forces may be written as (*1, 11, 22, 33*)

$$\underline{N_i} = -\sum_j D_{ij} \nabla C_j + \underline{V} C_i, \quad i = 1, .., n-1 \tag{2}$$

All summations are from 1 to $n - 1$ in the above and in subsequent equations.

For present purposes the reference frame need not be specified, for Equation (2) is valid in all common reference frames, a change of reference frame merely changes the values of the diffusion coefficients. Consequently the reference velocity $\underline{V}$ can be taken to be any one of the usual reference velocities, molar, mass, volume average, etc. Equations for the conversion of the diffusion coefficients from one reference frame to another are available (*11, 22, 33*).

The concentration in Equation (2) can be expressed either in mass per unit volume or moles per unit volume with corresponding mass or molar units for the flux.

Equation (2) contains $(n - 1)^2$ diffusion coefficients, but the Onsager reciprocal relationships (*24*) indicate that only $n(n - 1)/2$ are independent. The D_{ii} are termed "main diffusion coefficients" and the D_{ij} $(i \neq j)$ "cross diffusion coefficients." In general $D_{ij} \neq D_{ji}$, and these cross diffusion coefficients may be positive or negative. The main diffusion coefficients however are expected to always be positive.

The cross diffusion coefficients in gases may be greater or less than the main coefficients, usually less, while available information concerning liquids indicates that (*3, 7, 8, 9, 10, 12, 13, 26, 34, 35*) the cross coefficients are generally smaller than the main coefficients. Since a component with negligibly small cross coefficients obeys Fick's law, the interaction effects to be studied here usually will be more pronounced in gases than in liquids.

In ideal gas mixtures these diffusion coefficients may be obtained from the kinetic theory of gases [the Maxwell-Stefan equations (*23*)] in terms of the binary diffusion coefficients and composition. In nonideal gases, liquids and solids the diffusion coefficients must be measured. Measurements have been carried out only in ternary mixtures, but there is no reason to expect Equation (2) not to apply in general, since it depends only upon the assumption that the fluxes are linear functions of the chemical potential (or concentration) gradients.

In the literature on liquid diffusion the diffusion coefficients in Equation (2) are referred to as the *practical diffusion coefficients* (*11, 22*) since they are measured in the usual experiments. Other diffusion coefficients may be defined by replacing the concentration gradients in Equation (2) by other related gradients such as chemical potential gradients; but as pointed out earlier (*27*) the present formulation is also practical in engineering work, for once the practical diffusion coefficients are known, Equation (2) gives a complete description of the relation between the fluxes and concentration gradients. It will also be seen that the multicomponent diffusion equations can be reduced to a set of equivalent binary equations which are easily solved when the Equation (2) formulation is used. Indeed this is why the practical diffusion coefficients are practical, for the experimental methods are based upon special cases of the solution obtained here (*3, 12*).

REDUCTION OF EQUATIONS TO BINARY FORM

An examination of the limiting forms of the diffusion coefficients in Equation (2) at the borders of the concentra-

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tion field indicates that the coefficients must in general be concentration dependent [the results are given by Shuck and Toor for a ternary mixture (*26*), but they are easily generalized]. In the following development it is assumed that the concentration changes are small enough so that the diffusion coefficients may be treated as constants over the range of concentration attained. The result of this linearized theory will only be exact for small changes in concentration, but it will be seen that the errors caused by the assumption do not appear to be serious, even for large changes in concentration.

Thus the equation to be solved is from Equations (1) and (2)

$$\frac{\partial C_i}{\partial \theta} + \nabla \cdot (\underline{V}\, C_i) = \sum_j D_{ij} \nabla^2 C_j + r_i, \quad i = 1, .., n-1 \tag{3}$$

Equation (3) represents a set of $n - 1$ equations which are coupled through the cross diffusion coefficients and possibly through the reaction terms. It is the coupling by the cross diffusion coefficients which gives rise to the essential difference between binary and multicomponent mass transfer and which is of primary interest here.

This coupling will be removed by a device similar to that used by Henry (*15, 16*) to solve a problem in which the energy equation was coupled with the binary diffusion equation [see also Crank (*6*)].

Multiplying each of Equations (3) by the undetermined constant s_i and summing one gets

$$\frac{\partial (\sum_i s_i C_i)}{\partial \theta} + \nabla \cdot \underline{V} (\sum_i s_i C_i) = \nabla^2 (\sum_i \sum_j s_i D_{ij} C_j) + \sum_i s_i r_i \tag{4}$$

If this equation is to reduce to a binary form, the s_i must be chosen so that

$$\sum_i \sum_j s_i D_{ij} C_j = D \sum_i s_i C_i = D \sum_j s_j C_j \tag{5}$$

where D must be independent of concentration.

Interchanging the order of summation on the left and equating coefficients of the independent C_j one obtains

$$\sum_i s_i D_{ij} - s_j D = 0, \quad j = 1, .., n-1 \tag{6}$$

Equation (6) represents a system of $n - 1$ linear, homogeneous equations, so a solution exists only if

$$|D_{ij} - D\,\delta_{ij}| = 0 \tag{7}$$

This determinant is an algebraic equation of degree $n - 1$ in D. Accordingly there are $n - 1$ roots, say, $D_1, D_2, \ldots, D_{n-1}$, and for each root $D = D_k$, Equation (6) can be solved for all but one of the s_i in terms of the remaining s_i. If the values of s_i corresponding to the root D_k are written as s_{ik}, then from Equation (6) the s_{ik} are obtained by solving the system of linear equations

$$\sum_i s_{ik} D_{ij} = s_{jk} D_k, \quad j = 1, .., n-1 \tag{8}$$

for $k = 1, 2, \ldots, n - 1$. If the s_{kk} are set equal to 1, then all the remaining s_{ik} may be determined from Equation (8).

Substituting Equation (5) into Equation (4) and using the subscript k one gets

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

where

$$\psi_k = \sum_i s_{ik} C_i, \quad k = 1, .., n-1 \tag{10}$$

$$R_k = \sum_i s_{ik} r_i, \quad k = 1, .., n-1 \tag{11}$$

$$s_{kk} = 1, \quad k = 1, .., n-1 \tag{12}$$

Equation (9) represents $n - 1$ binary diffusion equations in the $n - 1$ linear combinations of the $n - 1$ independent concentrations. Each linear combination or combine behaves as if it were a component of a binary mixture in which the diffusion coefficient (or diffusivity) is D_k and the rate of reaction is R_k.

Defining the combine fluxes analogously to the component fluxes in a binary mixture

$$\underline{\eta}_k = - D_k \nabla \psi_k + \underline{V}\, \psi_k, \quad k = 1, .., n-1 \tag{13}$$

allows Equation (9) to be written as

$$\frac{\partial \psi_k}{\partial \theta} + \nabla \cdot \underline{\eta}_k = R_k, \quad k = 1, .., n-1 \tag{14}$$

It can be shown by use of Equations (13), (10), (8), and (2) that a consequence of the definition of $\underline{\eta}_k$ is the relationship

$$\underline{\eta}_k = \sum_i s_{ik} \underline{N}_i, \quad k = 1, .., n-1 \tag{15}$$

Thus the combine fluxes are related to the component fluxes the same way that the combine concentrations are related to the component concentrations.

Equations (9), (13), and (14) can all be obtained from the binary diffusion equations by the simultaneous transformations

$$C_k^o \rightarrow \psi_k \tag{16a}$$

$$\underline{N}_k^o \rightarrow \underline{\eta}_k \tag{16b}$$

$$D_k^o \rightarrow D_k \tag{16c}$$

$$r_k^o \rightarrow r_k \tag{16d}$$

$$\underline{V}^o \rightarrow \underline{V} \tag{16e}$$

where k takes on values from 1 to $n - 1$, so the above transformations may be applied to the solutions to the equivalent binary problems to give the solution to the multicomponent problem. The transformations apply to time average as well as instantaneous quantities in turbulent flow.

If the initial and boundary concentrations are constant, the set of equivalent binary problems represents one binary solution with a different diffusion coefficient for each value of the index k.

The boundary conditions for Equation (9) may be divided into two kinds. The first consists of those problems in which the component concentrations or fluxes are prescribed at the boundaries; hence by Equations (10) and (15) the combine concentrations or fluxes are also prescribed and the equivalent binary problem may be identified immediately.

With the second kind of boundary conditions the component concentrations and/or fluxes are given indirectly at the boundary. Generally for this kind the boundary conditions of the equivalent binary problem cannot be determined without solving Equation (9).

The rate of reaction depends upon one or more of the concentrations, and since the C_i may be written as linear combinations of the ψ_k [see Equation (18)]

$$R_k = R_k (\psi_1, \psi_2, .., \psi_{n-1}), \quad k = 1, .., n-1 \tag{17}$$

Consequently even if only one of the components reacts, and even if this reaction rate depends upon only one of the concentrations, all the combines react and the reaction rates depend upon all the combine concentrations.

Hence if a reaction takes place the combines are coupled through the reaction terms so the solution to the equivalent binary problem will not normally be available and it will be necessary to solve Equation (9) directly.

The combines are also coupled implicitly through the equations of motion if the mixture viscosity and density depend upon concentration, and these quantities must be assumed to be constant if the equivalent binary problem is to be identified without solving the coupled equations. If viscosity and density can be taken as constant, then for large fluxes the velocity field depends upon the diffusion process, but only through the velocity at the boundary, and in this case the equivalent binary problem may be readily identified.

INVERSIONS AND VALIDITY OF THE METHOD

After the D_k and s_{ik} are obtained from Equations (7) and (8), respectively, and the solution to Equation (9) is obtained, the component concentrations and fluxes must be recovered from the combine concentrations and fluxes by inverting Equations (10) and (15). The result is

$$C_i = \sum_k S_{ik}\,\psi_k/|s_{ik}| \qquad (18)$$

$$\underline{N_i} = \sum_k S_{ik}\,\underline{\eta_k}/|s_{ik}| \qquad (19)$$

where S_{ik} is the cofactor of the element s_{ik} in the determinant $|s_{ik}|$.

The above inversions may not be possible if $|s_{ik}|$ is zero.* In ternary mixtures of ideal gases it will be shown that it can never be zero (except for trivial cases), and this also appears to be true in the ternary liquid systems studied so far. It is assumed that $|s_{ik}| \neq 0$.

Furthermore all the D_k must be positive numbers (or if the D_k are complex the real parts must be positive) for the method of solution to be meaningful, for if any D_k is negative the essential nature of multicomponent system cannot be described by equations which neglect the concentration dependence of the practical diffusion coefficients.

It will be seen that the D_k can be obtained as positive, real numbers in all known ternary systems, and it is possible that most if not all multicomponent systems will behave in this fashion.*

It follows from Equations (18) and (16*a*) that the component concentrations in a multicomponent system are linear functions of the concentrations in the equivalent binary problems. Equations (19) and (16*b*) give similar results for the fluxes. The consequences of these results will be examined later.

THREE-COMPONENT MIXTURES

In this section explicit forms of the parameters are obtained for a three-component mixture. Equation (7) gives

$$(D_{11} - D)(D_{22} - D) = D_{12}D_{21} \qquad (20)$$

$$2D_{1,2} = D_{11} + D_{22} \pm \sqrt{(D_{11} - D_{22})^2 + 4D_{12}D_{21}} \qquad (21)$$

and noting that as D_{12} or D_{21} tends to zero one root tends to D_{11} and one to D_{22}, one may for convenience choose D_i as the root which tends to D_{ii} as D_{12} or D_{21} tends to zero. The larger D_i then corresponds to the larger D_{ii}.

From Equation (21)

$$D_1 + D_2 = D_{11} + D_{22} \qquad (22)$$

Equation (8) gives

$$s_{ij} = \frac{D_j - D_{jj}}{D_{ij}} = \frac{D_{ii} - D_i}{D_{ij}}, \quad i, j = 1, 2 \quad j \neq i \qquad (23)$$

and these equations yield

$$|s_{ik}| = \frac{D_1 - D_2}{D_1 - D_{22}} = \frac{D_1 - D_2}{D_{11} - D_2} \qquad (24)$$

From the definition of S_{ik}

$$S_{ii} = 1, \quad i = 1, 2 \qquad (25a)$$

$$S_{ij} = -s_{ji}, \quad i, j = 1, 2 \quad j \neq i \qquad (25b)$$

One wishes to show that D_1 and D_2 are real positive numbers and that $|s_{ik}|$ is not zero.* From Equations (21) and (24) it follows that both conditions are satisfied if D_1 and D_2 are distinct as well as real and positive.

One instance in which the roots are not distinct occurs when $D_{11} = D_{22}$ and D_{12} and/or D_{21} is zero. From a result given by Burchard and Toor (3) one can conclude that either this condition can be removed by proper choice of the independent species, or if it cannot be removed then both D_{12} and D_{21} are zero. Since the second conclusion represents a trivial situation, this particular limit causes no difficulty.

The D_{ij} are known for ideal gas mixtures, and if the reference velocity is taken to be the molar average velocity the D_{ij} are

$$D_{ii} = \mathcal{D}_{i3}\,[(1 - y_i)\,\mathcal{D}_{ij} + y_i\,\mathcal{D}_{j3}]/S \qquad (26a)$$

$$D_{ij} = y_i\,\mathcal{D}_{j3}\,(\mathcal{D}_{i3} - \mathcal{D}_{ij})/S \qquad (26b)$$

$$S = y_1\,\mathcal{D}_{23} + y_2\,\mathcal{D}_{13} + y_3\,\mathcal{D}_{12} \qquad (26c)$$

The binary diffusion coefficients are of course real positive numbers, and $\mathcal{D}_{ij} = \mathcal{D}_{ji}$. By substituting the values from Equation (26) into Equation (21) it can be shown that if the components are chosen so that $\mathcal{D}_{12}$ is the smallest of the three $\mathcal{D}_{ij}$, then the D_k are always real, positive, and distinct for all but trivial situations. Hence in three-component mixtures which obey the Maxwell-Stefan equations the combines can always be made to behave like the components of an ordinary binary mixture.

The practical diffusion coefficients in ideal gas mixtures of more than three components can be obtained from the Maxwell-Stefan equations (23). The calculations although tedious merely require a straightforward inversion from the Maxwell-Stefan form to the form of Equation (2).

General conclusions concerning even ternary liquid mixtures are difficult to obtain, but in all systems in which the D_{ij} have been measured with sufficient accuracy to allow conclusion to be drawn the D_k are indeed real, positive, and distinct (*7, 8, 9, 10, 12, 13, 26, 34, 35*).

If the cross diffusion coefficients in liquids are much less than the main coefficients, and the difference between the main coefficients is small, as the data obtained so far indicate, Equation (21) shows that the D_k will never be negative. They may be complex, but the real parts will always be positive; if this is the case, the procedure which has been developed will be valid even though the equivalent binary problems will have complex diffusion coefficients.

It is assumed below that the D_k are all real, positive, and distinct for any number of components. This insures that $|s_{ik}| \neq 0$. The exceptional case of repeated roots will be treated at a later time.

RATE EQUATIONS

In this section the multicomponent rate equations are obtained for situations in which there is no reaction. It is assumed at first that the fluxes are small so that the veloc-

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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 inversion will always be possible, and the D_k will be real positive numbers.

ity field does not depend upon the diffusion process. In addition, although the general results are valid for both kinds of boundary conditions, the discussion in this and the following section is restricted to problems in which the boundary conditions are of the first kind.

The rate of transfer across the boundary in the equivalent binary system may be written as

$$N^o_{kI} = k^o_k \, \Delta \, C^o_k \qquad (27)$$

where k^o_k is the local or average binary mass transfer coefficient which depends upon some or all the quantities, diffusion coefficient, form of the initial and boundary conditions, position, time, geometry, hydrodynamics, viscosity, and density, and ΔC^o_k is the appropriate driving force.

The rates of transfer of the combines are obtained by applying Equation (16) to Equation (27):

$$\eta_{kI} = k_k \, \Delta \, \psi_k, \quad k = 1, .., n-1 \qquad (28)$$

k_k is the binary mass transfer coefficient in the system in which the binary diffusion coefficient is D_k. As mentioned earlier if the boundary and initial concentrations are constant, the k_k in Equation (28) will differ from each other only in that each coefficient will be evaluated with a different diffusion coefficient.

Substituting Equation (28) into Equation (19) and then using Equation (10) one obtains

$$N_{iI} = \frac{\sum\limits_{l}\sum\limits_{k} S_{ik} \, s_{lk} \, k_k \, \Delta \, C_l}{|s_{ik}|}, i = 1, .., n-1 \qquad (29)$$

which can be written as

$$N_{iI} = \sum_{l} k_{il} \, \Delta \, C_l, \quad i = 1, .., n-1 \qquad (30)$$

where

$$k_{il} = \frac{\sum\limits_{k} S_{ik} \, s_{lk} \, k_k}{|s_{ik}|}, \quad i, l = 1, .., n-1 \qquad (30a)$$

It can be shown from Equations (8) and (31) that the D_{il} are related to the D_k in exactly the same way the k_{il} are related to the k_k. This basic relationship leads naturally to the definition of the k_{il} as multicomponent mass transfer coefficients, with k_{ii} the main coefficients and k_{il}, $i \neq l$ the cross coefficients.

Since the s_{ik} and their cofactors are related by the equation

$$\sum_{k} S_{ik} \, s_{lk} = |s_{ik}| \, \delta_{il}, \quad i, l = 1, .., n-1 \qquad (31)$$

Equation (29) may also be written in the form

$$N_{iI} = k_i \, \Delta \, C_i + \frac{1}{|s_{ik}|} \sum_{l}\sum_{k} S_{ik} \, s_{lk} \, (k_k - k_l) \, \Delta \, C_l, \qquad i = 1, .., n-1 \quad (32)$$

When all the cross diffusion coefficients go to zero there is no coupling, the cross mass transfer coefficients in Equation (30*a*) as well as the series in Equation (32) go to zero, and Equations (29), (30), and (32) reduce to the binary equation. Hence either the cross coefficients in Equation (30) or the series in Equation (32) may be considered to represent the coupling.

It is seen that in the usual case in which the cross diffusion coefficients are not zero all the fluxes depend upon all the driving forces, so the coupling or interaction phenomena which occur in steady unidirectional diffusion (diffusion barrier, osmotic diffusion, reverse diffusion) take place to a greater or lesser extent in all multicomponent mass transfer. This has been found to be true experimentally (*32*) and has been predicted by various models (*31*). The above equations however do not require the assumption of any particular model of the transport process. This is fortunate, for it means that the multicomponent fluxes may be obtained without a detailed knowledge of the mass transfer process; an empirical equation for the binary mass transfer coefficient is sufficient.

If the system is made overdeterminate, say by setting the flux of certain components zero at the boundary, then for each flux which is zero Equation (29) or (30) or (32) gives one relationship among the ΔC_l indicating that one concentration cannot be fixed, and the ΔC_l corresponding to the zero flux can be eliminated from the set of equations. If all but one flux is zero, all the corresponding ΔC_l can be obtained in terms of the concentration difference of the component with the nonzero flux, so Equation (29) merely reduces to a form like the binary equation, Equation (27). It is only in degenerate problems of this type that the effective diffusivity concept is meaningful.

For a ternary system Equation (32) with Equations (20) to (25) gives

$$N_{iI} = k_i \, \Delta \, C_i + \frac{k_i - k_j}{D_i - D_j} \left[(D_{ii} - D_i) \, \Delta \, C_i + D_{ij} \, \Delta \, C_j \right], \qquad \begin{matrix} i, j = 1, 2 \\ j \neq i \end{matrix} \quad (33)$$

If D_{ij} approaches zero, D_i approaches D_{ii} and component i diffuses independently of component j, although j remains coupled to i. A few common situations are examined below.

Film

For steady unidirectional diffusion through a film $k_k = D_k/L$, and with Equations (8) and (30) Equation (32) reduces to the simple form

$$N_{iI} = \frac{1}{L} \sum_{j} D_{ij} \, \Delta \, C_j, \quad i = 1, .., n-1 \qquad (34)$$

a result which also follows directly from Equation (2).

Penetration

For unsteady diffusion across an interface where the concentrations are C_{lI}, constant for time greater than zero, into a medium with constant initial concentrations C'_l, the instantaneous mass transfer coefficient of combine k is $\sqrt{D_k/\pi\theta}$ and ΔC_l is $(C_{lI} - C'_l)$. Equation (32) then shows that all the fluxes are inversely proportional to the square root of time and that the coupling is weaker than that obtained in steady diffusion through a film.

Forced Convection

The mass transfer coefficient of combine k is given for a wide range of conditions by

$$\frac{k_k}{U} \left(\frac{\mu}{\rho \, D_k} \right)^m = g \left(N_{Re}, \frac{x}{\mathcal{L}} \right), k = 1, .., n-1 \qquad (35)$$

so Equation (31) may be written

$$\frac{N_{iI}}{U \, g} = \left(\frac{\mu}{\rho \, D_i} \right)^{-m} \Delta C_i + \frac{\sum\limits_{l}\sum\limits_{k} S_{ik} \, s_{lk} \left[\left(\frac{\mu}{\rho \, D_k} \right)^{-m} - \left(\frac{\mu}{\rho \, D_l} \right)^{-m} \right] \Delta C_l}{|s_{ik}|}, \qquad i = 1, .., n-1 \quad (36)$$

Equation (36) includes the laminar and turbulent boundary-layer problems, the Greatz problem as well as its turbulent analogue, transfer in packed columns, distillation columns, etc. It should be particularly useful in multicomponent distillation where the molar average reference velocity is zero at the interface.

Since m in Equation (36) varies from 1 for steady, unidirectional molecular diffusion to near zero for totally turbulent

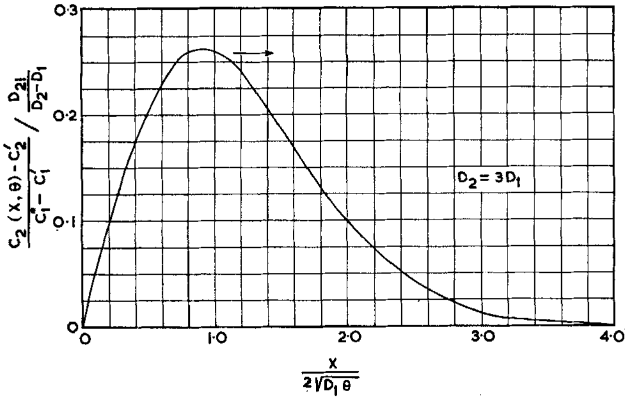

Fig. 1. Concentration profile of initially undisturbed component, semi-infinite medium.

transport, for a given multicomponent mixture the maximum coupling occurs in the former case and the minimum coupling in the latter case. Thus the strength of the coupling in mass transfer depends both upon the practical diffusion coefficients and on the value of m.

An important result brought out by Equation (36) is that convection, laminar or turbulent, affects only the combine mass transfer coefficients, not the s_{ik} and S_{ik} which depend only upon the D_{ij}.

The above results may also be applied to high fluxes if the D_{ij}, mixture viscosity, and density may be taken as constant. The k_k will then depend upon the reference velocity at the interface and the terminal concentrations. The results will be less accurate than before because of the greater variations in physical properties.

Alternate forms of the high flux equations are also possible. For example if the effect of a high flux in the equivalent binary problem is the same as it would be if a film were present, then application of Equation (16) to the binary filmlike solution (2) and use of Equations (10) and (15) yields

$$N_I = k_k C \ln \frac{\sum_i s_{ik} \, (N_{iI}/N_I - \overline{C}_i/C)}{\sum_i s_{ik} \, (N_{iI}/N_I - C_{iI}/C)}, \quad k = 1, \ldots, n-1 \tag{37}$$

where k_k is the mass transfer coefficient of combine k at a low flux. With a determinancy condition these equations can be solved for the fluxes at the interface.

CONCENTRATION PROFILES FOR SMALL FLUXES

The concentration profiles which correspond to Equation (27) can usually be written in the form

$$\frac{\Delta C^o{}_k}{\Delta C^o{}_{ko}} = f^o{}_k \, (x, y, z, \theta) \tag{38}$$

where $f^o{}_k$ also generally depends upon $D^o{}_k$, hydrodynamics, etc. $\Delta C^o{}_k$ is now the displacement from equilibrium at x, y, x, θ, and $\Delta C^o{}_{ko}$ is some characteristic displacement. Equations (16) and (38) yield

$$\frac{\Delta\psi_k}{\Delta\psi_{ko}} = f_k \, (x, y, z, \theta) \tag{39}$$

where f_k is $f^o{}_k$ evaluated with $D^o{}_k = D_k$. Equations (18) and (10) convert this equation into a form like Equation (29):

$$\Delta C_i = \frac{\sum_l \sum_k S_{ik} \, s_{lk} \, f_k \, \Delta C_{lo}}{|s_{ik}|}, \quad i = 1, \ldots, n-1 \tag{40}$$

With Equation (31) one obtains the form analogous to Equation (32):

$$\Delta C_i = \Delta C_{io} \, f_i + \frac{\sum_l \sum_k S_{ik} \, s_{lk} \, (f_k - f_l) \, \Delta C_{lo}}{|s_{ik}|}, \quad i = 1, \ldots, n-1 \tag{41}$$

If transient processes are considered, paraphrasing Henry (*15*) it may be said that the first term on the right represents the wave which would result if there were no coupling between the diffusion processes and which may be referred to as the *permanent wave*. The remaining terms represent the result of coupling and may be called the *temporary waves* since they start at time zero, increase to a maximum, and then fall to zero again.

The earlier rate equations can of course be obtained from the above solutions. However in many practical situations the $f^o{}_k$ are unknown, even though the $k^o{}_k$ are known from experiment. Hence the rate equations have been obtained separately to emphasize the fact that transfer rates in multicomponent systems can be predicted even when the $f^o{}_k$ are unknown.

With Equations (20) to (25) the ternary form of Equation (41) is found to be

$$\Delta C_i = \Delta C_{io} \, f_i + \frac{f_i - f_j}{D_i - D_j} \, [(D_{ii} - D_i) \, \Delta C_{io} + D_{ij} \, \Delta C_{jo}], \quad \begin{matrix} i, j = 1, 2 \\ j \neq i \end{matrix} \tag{42}$$

A special case of Equation (42) was obtained directly by Fujita and Gosting (*12*) for a case of free diffusion and was used in the measurement of the D_{ij}.

An alternate form of Equation (42) is

$$\Delta C_1 = \phi_1 + \frac{D_{11} - D_1}{D_{21}} \, \phi_2 \tag{43a}$$

$$\Delta C_2 = \phi_2 + \frac{D_{22} - D_2}{D_{12}} \, \phi_1 \tag{43b}$$

$$\phi_i = \frac{[(D_{ii} - D_j) \, \Delta C_{io} + D_{ij} \, \Delta C_{jo}]}{D_i - D_j} \, f_i, \quad \begin{matrix} i, j = 1, 2 \\ j \neq i \end{matrix} \tag{43c}$$

Again considering transient processes and paraphrasing Henry (*15*), each diffusion wave of species i is accompanied by a subsidiary diffusion wave of species j whose magnitude is proportional to that of species i, the relation between the two depending only upon the practical diffusion coefficients (and the ΔC_{io}). Even if only one of the independent boundary concentrations is altered, there will nevertheless be the complete set of two diffusion waves for each component. A similar form exists for the n component system.

For steady, unidirectional molecular diffusion through a film f_k is x/L, and Equation (40) or (41) takes on the elementary form

$$\Delta C_i = \Delta C_{io} \frac{x}{L}, \quad i = 1, \ldots, n-1 \tag{44}$$

Other forms of f_k may be obtained in standard works, and two examples are shown graphically.

PENETRATION

A mixture of components 1, 2, and 3 of concentrations C'_1, C'_2, C'_3 extends from $x = 0$ to $x = \infty$, and at time zero the concentration of component 1 at $x = 0$ is changed to $C_1{}^*$ while the concentration of component 2 at $x = 0$ is unchanged, $C_2{}^* = C'_2$. C is constant, and the reference velocity is zero. Among other things this corresponds to an ideal gas mixture at a constant temperature and pressure.

The concentrations for time greater than zero are given by Equation (42) or (43), and the component 2 concentration becomes

$$\frac{C_2(x,\theta) - C'_2}{C_1^* - C'_1} = \frac{D_{21}}{D_2 - D_1}\left(\operatorname{erf}\frac{x}{2\sqrt{D_1\theta}} - \operatorname{erf}\frac{x}{2\sqrt{D_2\theta}}\right) \tag{45}$$

Figure 1 shows the component 2 wave for $D_2 = 3\,D_1$. Since the amplitude is constant, the disturbance moves into the medium without decaying (at a rate proportional to $1/\sqrt{\theta}$). The concentration of component 1 is a linear combination of the profile in the figure and the usual error function profile.

EXTENDED SOURCE

A mixture of components 1, 2, and 3 of concentration C_1^*, C_2^*, C_3^* extends from $-\infty$ to $+\infty$ and at time zero the concentration of component 1 in the region $-a < x < a$ is changed to $\hat{C}_1$, while the concentration of component 2 is unchanged. Again C is constant, and the reference velocity is zero. As before Equation (42) or (43) gives the concentrations for time greater than zero. The equation for $C_2\,(x, t)$ takes on a form like Equation (45) with f_i now given as the sum of two error functions (6).

Figure 2 gives the C_2 profile with $D_2 = 3D_1$. Two waves move out from the interface, one in each direction. Eventually a crater with a raised rim forms. In the early stages the crater deepens and the rim grows higher and wider, but as time progresses and the crater widens it gets shallower and the rim lowers until finally the concentration returns to its initial equilibrium value.

The above figures correspond roughly to a gas mixture made up of equal volumes of carbon dioxide, water, and hydrogen, components 1, 2, and 3, respectively. In this mixture D_2 is about $3D_1$, and $D_{21}/(D_2 - D_1)$ is about one half; also D_{12} is close to D_{21}.

It is noted that if the initial water concentration is the saturation value, then in the second example supersaturation or condensation will take place, while in the first example this will only occur if the carbon dioxide concentration at the interface is greater than the initial carbon dioxide concentration.

Concentration profiles for large fluxes may be obtained in the same manner as above if physical properties are constant. For steady state diffusion through a film for example the f_k in Equation (40) or (41) are given by

$$f_k = \frac{\exp\,(N_I x/D_k C) - 1}{\exp\,(N_I L/D_k C) - 1}, \quad k = 1,\ldots, n-1 \tag{46}$$

DIAPHRAGM CELL

Although it does not follow directly for Equation (9), the solution for the quasi steady state diaphragm cell is of some interest. The equation for the instantaneous difference between the two halves when there is no volume change on mixing and a volume average reference velocity is used is

$$\frac{d(\Delta C_i)}{d\theta} = -\beta \sum_j D_{ij}\,\Delta C_j, \quad i = 1,\ldots, n-1 \tag{47}$$

This equation is obtained from Equation (34) and material balances (3).

By exactly the same procedure as before this becomes

$$\frac{d(\Delta\psi_k)}{d\theta} = -\beta\, D_k\,\Delta\psi_k, \quad k = 1,\ldots, n-1 \tag{48}$$

Solving and inverting as before one gets

$$\Delta C_i = \frac{\sum\limits_l \sum\limits_k S_{jk}\, s_{lk}\, e^{-\beta D_k \theta}\,\Delta C_{lo}}{|s_{ik}|}, \quad i = 1,\ldots, n-1 \tag{49}$$

The above result for a three-component system was obtained directly by Burchard and Toor (3) and has been used in measuring the D_{ij}. Hence both of the methods which have been used to measure the D_{ij} in liquids are based on the present linearized theory. It is to be hoped that the general solutions now available might lead to new methods of measurement.

A HINDSIGHT METHOD OF SOLUTION

Since Equation (40) can be written as

$$\Delta C_i = \sum_k A_{ik} f_k, \quad i = 1,\ldots, n-1 \tag{50}$$

with

$$A_{ik} = \frac{\sum\limits_l S_{ik}\, s_{lk}\,\Delta C_{lo}}{|s_{ik}|}, \quad i, k = 1,\ldots, n-1 \tag{51}$$

an alternate method of solution of Equation (3) is to assume Equation (50) to be the solution and to solve for the A_{ik} directly. It is interesting to follow this new path even though it leads to the same solution as before.

Assume Equation (50) to be the solution to Equation (3), and for simplicity let there be no reaction and $\nabla \cdot \underline{V} = 0$. The f_k then are assumed to satisfy the equations

$$\frac{\partial f_k}{\partial \theta} + \underline{V} \cdot \nabla f_k = D_k \nabla^2 f_k, \quad k = 1,\ldots, n-1 \tag{52}$$

and suitable boundary conditions. Substituting Equation (50) into (3) and using Equation (52) one obtains

$$\sum_j D_{ij} A_{jk} = A_{ik} D_k, \quad i = 1,\ldots, n-1 \tag{53}$$

a set of equations much like Equation (8) which has a solution only if Equation (7) is satisfied. Hence the D_k are the combine diffusion coefficients. Since for each k Equation (53) sets only the ratios of the A_{ik}, there are still $n - 1$ arbitrary constants to be chosen to fit the boundary conditions. Suppose for example these boundary conditions are

$$\Delta C_i\,(x, y, z, 0) = \Delta C_{io} \tag{54a}$$

$$\Delta C_i\,(b, \theta) = 0 \tag{54b}$$

$$\frac{\partial C_i}{\partial n}\,(B, \theta) = 0 \tag{54c}$$

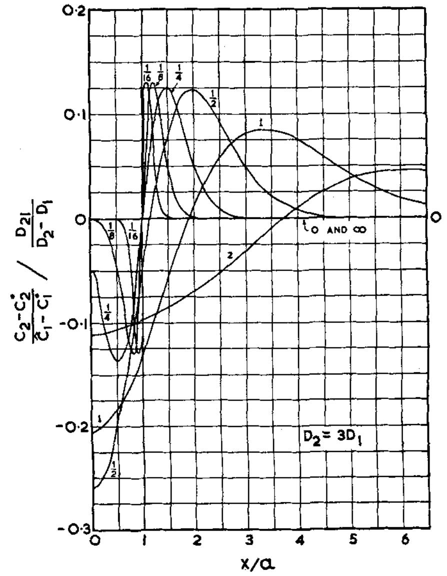

Fig. 2. Concentration profiles of initially undisturbed component, extended source, infinite medium. Numbers on graph are values of $\sqrt{D_1\theta/a^2}$.

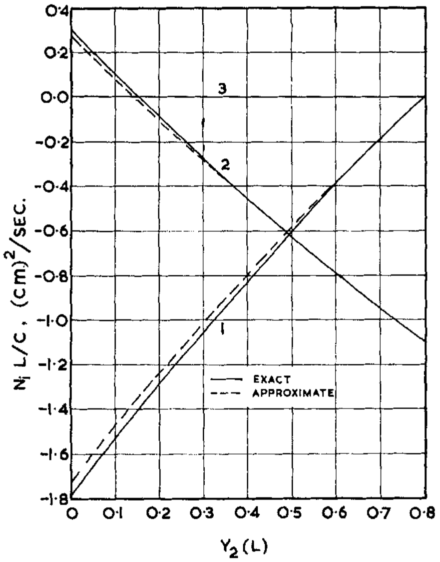

Fig. 3. Comparison of approximate and exact fluxes.

$1 = H_2O$, $2 = CO_2$, $3 = H_2$
$Y_1(0) = 0.0$ $\quad Y_1(L) = 0.8 - Y_2(L)$
$Y_2(0) = 0.7$ $\quad Y_2$ (L) varies

where b and B refer to two different boundaries of the system. Then from Equation (50) these are satisfied if

$$f_k(x, y, z, 0) = 1 \qquad (55a)$$

$$f_k(b, \theta) = 0 \qquad (55b)$$

$$\frac{\partial f_k}{\partial n}(B, \theta) = 0 \qquad (55c)$$

for $k = 1, 2 \ldots n - 1$, and

$$\sum_k A_{ik} = \Delta C_{io}, \quad i = 1, \ldots, n - 1 \qquad (56)$$

Thus Equation (55) defines the boundary conditions on the equivalent binary problem, and Equation (56) completely fixes the A_{ik} since it gives the $n - 1$ relationships needed to fix the $n - 1$ arbitrary A_{ik} which remain after the solution of Equation (53). But the A_{ik} given by Equation (51) also satisfy Equations (53) and (56). Hence both methods give the same solution.

COMPARISON WITH EXACT SOLUTIONS

The above solutions assume that the practical diffusion coefficients are constants. The concentration dependence of the practical diffusion coefficients and the coupling can be much larger in gases than in liquids (at least as far as is known), so a test of the assumption in gases is of most interest. Since exact solutions which account for the concentration dependence of the practical diffusion coefficients in ideal gases are available for simple situations, these are the solutions to the Maxwell-Stefan equations for steady unidirectional diffusion through a film, these results may be used for testing purposes.

Figure 3 shows a comparison of the rates predicted by Equation (37) with those given by Gilliland's solution (*5*) to the Maxwell-Stefan equations. The conditions are the same as given earlier (*29*) and cover a wide range of interactions. The practical diffusion coefficients used in the calculation were evaluated by using the arithmetic average of the terminal mole fractions in Equation (26). The check is good, even for the large concentration differences and hence large variations in the D_{ij} across the film.

Similar calculations for equimolal countercurrent diffusion [Equation (34)] gave even closer agreement with the exact solution (*29*) with mole fraction differences across the film as large as 1.0. (The results were almost indistinguishable from the exact solution on the scale of Figure 4 of reference *29*.)

In Figure 4 the concentration profiles calculated from Equations (26), (42), and (46) are compared with those given by Gilliland's equation. Again the practical diffusion coefficients were evaluated at the arithmetic average of the mole fractions at either end of the film. The terminal concentrations were assumed to be the same in both calculations, and the value of N_I used to compute each profile was computed from the corresponding rate equation. The approximate profiles are in good agreement with the exact ones.

The above results indicate that the errors caused by linearizing the diffusion equations are not serious for steady unidirectional diffusion in gases and imply that this will be true in general, but they give no information concerning the errors caused by neglecting variations in mixture density and viscosity under real conditions.

It should be noted that in ternary mixtures of ideal gases the practical diffusion coefficients cannot change sign as the composition changes, and this is expected to carry over to all ideal gas mixtures. However in highly nonideal liquid mixtures the signs of the cross diffusion coefficients may change with composition, and if this occurs the linearized equations will probably be of somewhat more restricted application. (As yet there is no proof that a sign change does occur.)

Calculations have also been carried out for turbulent flow in a tube with Equation (37) with the k_k given by the Colburn equation. The results are in closer agreement with models which attempted to account for the combined effects of molecular and turbulent transport (*31*) than with a film model (*31*), as is to be expected. On the basis of limited calculations the results appear to be in accord with the experiments which have been carried out (*32*).

The linearized theory would be of interest even if restricted to small changes in concentration, since it gives the essential behavior of multicomponent systems. The fact that it may yield accurate results even for large changes in concentration is encouraging, for higher accuracy will require facing the nonlinear characteristics of the differential equations.

BOUNDARY CONDITIONS OF THE SECOND KIND

When there is transfer between two phases or a reaction at a surface, the boundary conditions will generally

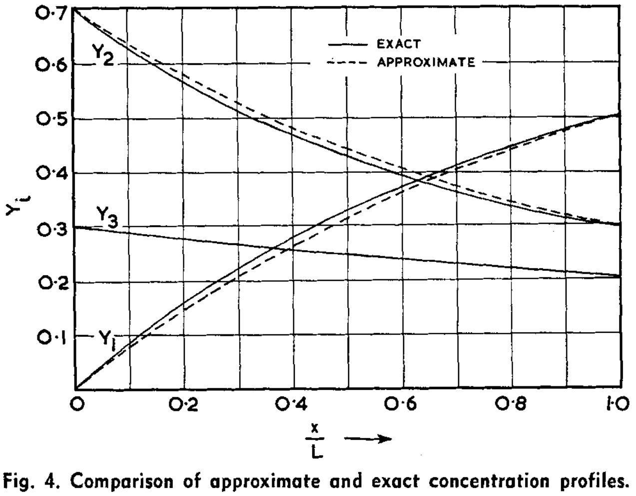

Fig. 4. Comparison of approximate and exact concentration profiles.

$1 = H_2O$, $2 = CO_2$, $3 = H_2$
$Y_1(0) = 0.0$ $\quad Y_1(L) = 0.504$
$Y_2(0) = 0.7$ $\quad Y_2(L) = 0.295$

	Exact	**Approx.**
N_1L/C	-1.050	-1.022
N_2L/C	-0.260	-0.265

be of the second kind. Then the combine concentrations at the boundary generally vary with time or distance, and the manner of variation can be obtained only by solving Equation (9) (written for each phase if need be) with the appropriate boundary conditions.

Hence although the general solutions [for example, Equations (29) and (40)] and conclusions which have been drawn are still valid, the actual values of the k_k and f_k must in this case be determined for each situation from Equation (9).

The effect of the varying boundary concentration on the mass transfer coefficient is almost always ignored in experimental work on binary systems and is ignored by the usual mass transfer models which assume a constant interfacial concentration.

Similarly for most practical situations it will probably be satisfactory to assume that the k_k do not depend upon the manner of variation of the interfacial concentrations. This assumption, which is included in all the usual mass transfer models, is considerably less restrictive than the choice of a particular model and allows application of the solutions obtained in this paper to the general multicomponent mass transfer problem under conditions for which physical properties may be treated as constant.

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NOTATION

a = half width of source
C = total concentation
C_i = concentration of component i
D = combine diffusion coefficient with single subscript, practical diffusion coefficient with double subscript
$\mathcal{D}_{ij}$ = binary diffusion coefficient
D^o = diffusion coefficient in equivalent binary system
f,g,G = functional symbols
k = mass transfer coefficient
k_i = multicomponent mass transfer coefficient
L = film thickness
$\mathcal{L}$ = characteristic length
m = exponent
n = number of components or distance normal to surface
N = total flux
N_i = flux of component i
N_{Re} = Reynolds number
r_i = rate of production of component i per unit volume by reaction
R_i = rate of production of combine i per unit volume by reaction
s_i, S_{ik} = constants
S = defined by Equation (26c)
S_{ik} = cofactor of s_{ik}
U = characteristic velocity
V = reference velocity
x = distance
y = distance
y_i = mole fractional of component i
z = distance

Greek Letters

β = cell constant
δ_{ij} = Kronecker delta
Δ = difference
η = combine flux
θ = time
μ = viscosity
ρ = density
ϕ = function defined by Equation (43)
ψ = combine concentration

Subscripts

i,j,k,l = indices
1,2,3 = components 1, 2, and 3
I = interface
o = characteristic value
— = vector

Superscripts

o = binary value
— = bulk average value
* = equilibrium value

Operators

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

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