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MASS AND ENERGY TRANSFER IN MULTICOMPONENT SYSTEMS

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In this paper, which is essentially an interpretative review, we develop the theory of multicomponent mass transfer using the Bird, Stewart and Lightfoot approach to binary mass transfer as a consistent basis. Methods of solving the coupled diffusion equations are discussed and procedures for estimating interphase mass transfer coefficients considered. The developed formalisms are applied to a few examples in the areas of distillation, condensation and extraction to demonstrate the importance of considering coupled diffusion effects in multicomponent transfers.

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George L. Standart Commemorative Issue

I. INTRODUCTION

Traditionally Fourier and Fick's laws have been used to describe the molecular transport processes of heat and mass. Fourier's law in the form

$$\mathbf{q} = -k_T \nabla T \tag{1}$$

is strictly valid for conduction of heat in an isotropic medium of uniform chemical composition and Fick's law

$$\mathbf{J}_i = -c\mathcal{D}_i \nabla x_i \tag{2}$$

is valid for isothermal, isobaric processes in an isotropic medium to the approximation of independent diffusion, i.e. each component in the mixture transfers independently and does not interact with other diffusing or non-diffusing species in the mixture. The approximation of independent diffusion can be strictly substantiated in three cases: (i) for binary diffusion, (ii) for diffusion of dilute species in a large excess of one of the components and (iii) for the case in which all the diffusion coefficients of all the components in the mixture can be regarded as equal.

Chemical engineers frequently have to deal with concentrated systems involving diffusion of several substances of widely differing properties, often with simultaneous heat transfer. This means that at each point in space and at each moment in time concentration gradients of several substances may exist together with a temperature gradient. Conventional approaches to the problem assume that the diffusive flux of each component depends on the gradient of its own composition and the heat flux only on the temperature gradient. As pointed out above this is strictly correct for certain special cases and in the general case we may expect the simplification of independent transfers to break down.

Unfortunately most experimental research works in the past have been limited to *binary* systems, although many, if not most, systems of practical interest are *multicomponent* (here we define a multicomponent system as one in which the number of components, $n \geqq 3$). The following questions naturally spring to mind:

(i) does the presence of three or more components in the system introduce additional complications unforseen from binary experiments alone ?,

(ii) if the answer to (i) is in the affirmative, how can the problem of multicomponent mass transport be tackled systematically? and

(iii) do the transport processes of mass and heat interact with each other in normal chemical engineering operations?

Though the first question has been in the minds of chemical engineers for a long time (Walter and Sherwood in 1941 raised doubts about the equalities of component efficiencies in multicomponent distillation), it is only during the last decade or so that almost complete answers to all three questions have become available, at least for non-reacting fluid systems.

In this review we consider correct formulations, and solutions, to the problem of intra- and interphase transfer of mass and energy in multicomponent fluid mixtures, limiting ourselves to systems in the absence of radiation and magnetic force fields.

Though fluid mixtures are treated exclusively in this review, the majority of the formalism presented here is applicable to solid phases as well. In most of the cases, the literature citations correspond to the more lucid reference rather than the historical 'first'.

In keeping with traditional chemical engineering literature (e.g. Bird, Stewart and Lightfoot, 1960†), the discussion of multicomponent transport phenomena is based on a *continuum* model for matter. In this model matter is assumed to be distributed continuously through space with the exception of surfaces of discontinuity (e.g. phase interfaces). The advantages of the continuum description over the more fundamental *particulate* (or *molecular*) model is that a general physical description is obtainable independent of choice of molecular models, of structures and interaction mechanisms and of assumptions of ideal solutions, etc. etc. The derivations of the general physical laws using continuum mechanics are much simpler and the derived relations of more general applicability. There is however a price to be paid for this simplicity and generality. Information is lost in a continuum picture and though the correct form of the constitutive relations are obtained, the coefficients in such equations have to be determined experimentally. The continuum approach is also called the *phenomen-*

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† Future references to this text will be abbreviated as BSL.

ological approach, since it describes the gross, observable, phenomena in nature. For a brilliant and detailed discussion on the foundations of continuum mechanics, the reader is referred to the treatise by Truesdell and Toupin (1960). The molecular or 'microscopic' approach is well summarized in Chapman and Cowling (1970) and Hirschfelder, Curtiss and Bird (1954).

II. ISOTHERMAL DIFFUSION IN n-COMPONENT MIXTURES

Consider the process of diffusion in a fluid mixture made up of n electrically neutral chemical constituents. If $\mathbf{u}_i$ represents the velocity of the ith species with respect to stationary (laboratory fixed) coordinate axes, the *molar flux* of that species denoting the number of moles passing through unit area per unit time is given by

$$\mathbf{N}_i = c_i\mathbf{u}_i, \qquad i = 1,2,\ldots n \tag{3}$$

The *mixture total molar flux* is obtained by summing equation (3) over the n species:

$$\mathbf{N}_t = \sum_{i=1}^{n} \mathbf{N}_i = \sum_{i=1}^{n} c_i\mathbf{u}_i = c\sum_{i=1}^{n} x_i\mathbf{u}_i \tag{4}$$

In defining the constituent and mixture total fluxes, we have used molar units because of their convenience in most chemical engineering calculations; the reader will find discussions in terms of mass units easy to parallel.

Now the flux of species i, $\mathbf{N}_i$, refers to a stationary coordinate frame of reference whereas the intrinsic process of diffusion refers to the movement of a particular constituent relative to the mixture. The reference velocity of the mixture may be defined in various ways (BSL, De Groot and Mazur, 1962; Lightfoot and Cussler, 1965; Slattery, 1972); here we use the molar average velocity:

$$\mathbf{u} = \sum_{i=1}^{n} x_i\mathbf{u}_i = \mathbf{N}_t/c \tag{5}$$

In many applications involving intra- and inter-phase mass transfer, the use of the molar average velocity is both simple and convenient.

We may therefore consider the *molar diffusion flux* defined with respect to the molar average velocity

$$\mathbf{J}_i \equiv c_i(\mathbf{u}_i - \mathbf{u}), \qquad i = 1,2,\ldots n \tag{6}$$

to provide a correct portrayal of the diffusion of species i through the mixture.

In view of equations (3)–(6), we may write the 'total' fluxes $\mathbf{N}_i$ in terms of a purely diffusive part (with respect to the molar average reference velocity) and a convective contribution due to the motion of the mixture as a whole,

$$\mathbf{N}_i = \mathbf{J}_i + c_i\mathbf{u} = \mathbf{J}_i + x_i\mathbf{N}_t, \qquad i = 1,2,\ldots n \tag{7}$$

The n diffusion fluxes $\mathbf{J}_i$ are not all independent for on summing (6) we find in view of equation (5) that

$$\sum_{i=1}^{n} \mathbf{J}_i = 0 \tag{8}$$

Now, the solution to any problem in multicomponent diffusion consists in determining the compositions and fluxes at every position in space and at every moment in time. This information is obtained by the solution of the differential equations describing the rate of change of concentration of species i in the mixture—the equations of continuity of species i (see BSL and Slattery, 1972 for derivations):

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (c_i \mathbf{u}_i) \equiv \frac{\partial c_i}{\partial t} + \nabla \cdot \mathbf{N}_i = 0, \qquad i = 1,2,\ldots n \tag{9}$$

Summing (9) over all the n constituent species, we obtain the differential equation expressing the conservation of total moles of mixture:

$$\frac{\partial c}{\partial t} + \nabla \cdot (c\mathbf{u}) \equiv \frac{\partial c}{\partial t} + \nabla \cdot \mathbf{N}_t = 0 \tag{10}$$

With definitions (3)–(6), the differential equations of continuity (9) may also be written as

$$c\frac{dx_i}{dt} \equiv c\left[\frac{\partial x_i}{\partial t} + \mathbf{u} \cdot \nabla x_i\right] = - \nabla \cdot \mathbf{J}_i, \qquad i = 1,2,\ldots n \tag{11}$$

where d/dt is the material derivative following the molar average mixture velocity.

Since the mole fractions add to unity:

$$\sum_{i=1}^{n} x_i = 1 \tag{12}$$

and the molar diffusion fluxes $\mathbf{J}_i$ sum to zero (cf. equation (8)), only $n-1$ of the equations (11) are independent and in order to solve them we need to relate the diffusion fluxes to the compositions x_i and/or the composition gradients ∇x_i in the system. Such relations are called *constitutive relations* for they describe the intrinsic diffusion behaviour of the particular system and material.

We now take up the problem of deciding what form these constitutive relations may take.

II.1 CONSTITUTIVE RELATIONS FOR MULTICOMPONENT DIFFUSION

II.1.a Generalized Fick's Law Formulation

Constitutive relations for diffusion in two-component systems are widely discussed in the literature (e.g. BSL). Thus for diffusion in a mixture made up of species 1 and 2, the diffusion flux of species 1 is most commonly written as a linear function of the composition gradient of component 1 as

$$\mathbf{J}_1 = -c\,\mathscr{D}_{12}\,\nabla x_1 \tag{13}$$

which is Fick's law of diffusion. We may write an analogous expression for the component 2 diffusion flux:

$$\mathbf{J}_2 = -c\,\mathscr{D}_{21}\,\nabla x_2 \tag{14}$$

but in view of equations (8) and (12) we see that the two binary diffusion coefficients are identical

$$\mathscr{D}_{12} = \mathscr{D}_{21} \tag{15}$$

Thus for a two-component system there is only one independent diffusion flux $\mathbf{J}_1$, only one independent composition gradient ∇x_1, only one independent diffusion coefficient $\mathscr{D}_{12}$ and only one independent constitutive relationship (13).

The diffusion coefficient $\mathscr{D}_{12}$ depends, in general, on the temperature, pressure and composition of the system but not on the composition *gradient*. This *linear* flux–composition gradient dependence has been found to hold even under extreme conditions (Laurence, 1966).

The situation with regard to an n-component system is more complex for now we have $n-1$ independent compositions, $n-1$ independent composition gradients and $n-1$ independent diffusion fluxes.

As a naive extension of the binary relation (13) we may first consider writing each diffusion flux as being proportional to its own composition composition gradient driving force, thus:

$$\mathbf{J}_i = -c\,\mathscr{D}_i\,\nabla x_i, \qquad i = 1,2,\ldots n \tag{16}$$

where $\mathscr{D}_i$ is some characteristic diffusion coefficient of species i in the mixture.

Summing (16) over the n species, we find in view of equation (8)

$$c\sum_{i=1}^{n} \mathscr{D}_i\,\nabla x_i = 0 \tag{17}$$

Since the n composition gradients sum to zero (cf. equation (12)):

$$\sum_{i=1}^{n} \nabla x_i = 0 \tag{18}$$

we may eliminate the nth gradient in equation (17) to obtain

$$c\sum_{i=1}^{n-1}(\mathcal{D}_i-\mathcal{D}_n)\nabla x_i=0 \tag{19}$$

Now, the $n-1$ composition gradients in (19) may all be varied independently and provided none of the $n-1$ independent species are infinitely dilute, the only solution possible to (19) is that all characteristic diffusion coefficients are identical (Toor and Arnold, 1965), i.e.

$$\mathcal{D}_i=\mathcal{D}_n, \qquad i=1,2,\ldots n-1 \tag{20}$$

Equation (20) requires each species in the n-component mixture to have equal facility for transfer irrespective of its molecular size and nature. We may expect such a simple result to be true when all the species making up the mixture are of similar nature and the solution is thermodynamically ideal. It has been found experimentally, for example, that diffusion in the ternary mixture toluene–chlorobenzene–bromobenzene is described adequately by *one* characteristic diffusion coefficient (Burchard and Toor, 1962).

For any constituent present in such low concentrations that not only $x_i\simeq 0$ but also $\nabla x_i\simeq 0$, $\mathcal{D}_i$ will not necessarily be equal to $\mathcal{D}_n$, e.g. in the diffusion of a number of very dilute solutes through a solvent, each solute diffuses independently with its own (binary) diffusivity with respect to the solvent $\mathcal{D}_{in}$.

For the general case of diffusion in non-ideal mixtures made up of components of differing size and nature present in significant concentrations we would not expect the simple result (20). We must therefore abandon the simple flux–driving force postulate (16) in the general case and be prepared to consider more general linear constitutive relations of the form

$$\mathbf{J}_i=-c\sum_{k=1}^{n-1}D_{ik}\nabla x_k, \qquad i=1,2,\ldots n-1 \tag{21}$$

in which we *postulate* that each flux is engendered by the composition gradients of all the independent species in the system, $n-1$ in number. Equations (21) represent the generalized Fick's law for multicomponent systems. The coefficients D_{ik}, of which there are $(n-1)^2$ in number, are called multicomponent diffusion coefficients.

Since mole fractions are directly measurable, the D_{ik} may be considered practical in the sense that they can be obtained from experimental measurements. No thermodynamic information concerning the non-ideality of the solution is required for their determination and none is required later when these coefficients are used to solve practical diffusion problems.

With a different choice of the mixture reference velocity, a different set of multicomponent diffusion coefficients is obtained. Methods for transforming one set of coefficients to another set are available in the literature (Lightfoot and Cussler, 1965; Toor, 1962).

The actual values of the D_{ik} in (21) also depend on the choice of the reference species n. In some cases the choice of the nth species is obvious: (i) an inert "solvent" through which the various "solute" components diffuse, (ii) a neutral mixture of the reacting species, etc. It is usual to label as solvent n in such cases the component in whose transfer we are not interested specifically. In many cases, as in the distillation of a mixture of hydrocarbons, the choice of the nth species has to be arbitrary.

In the interests of compactness and ease of manipulation, we shall find it convenient to represent the constitutive relations (21) in $n-1$ dimensional matrix notation as

$$(\mathbf{J}) = -c\,[D]\,(\nabla x) \tag{22}$$

where (J) is a column matrix of diffusion fluxes: $\mathbf{J}_1, \mathbf{J}_2 \ldots \mathbf{J}_{n-1}$; $[D]$ is a square matrix of diffusion coefficients, D_{ik} $(i,k = 1,2,\ldots n-1)$; (∇x) is a column matrix of composition gradients: $\nabla x_1, \nabla x_2, \ldots \nabla x_{n-1}$.

Equation (22) is the matrix analogue of the binary rate relation (13); we shall indeed discover that many multicomponent mass transfer relations can be written as matrix analogues of corresponding relations for two-component systems.

The constitutive relations (21), or (22), have been written down purely as formal linear generalizations of the binary Fick's law relationship (13). One might question whether composition gradients are the proper driving forces for diffusion. The theory of the Thermodynamics of Irreversible Proccesses (TIP) provides an answer to this question and at the same time gives a more fundamental basis for the treatment of multicomponent transport phenomena.

II.1.b Irreversible Thermodynamics of Diffusion

The purpose of the study of TIP, discussed in such texts as De Groot and Mazur (1962), Fitts (1962) and Haase (1969), is to extend classical thermodynamics to include systems in which irreversible (non-equilibrium) processes are taking place. Such an extension is made possible by assuming that for systems "not too far" from equilibrium the postulate of "local eequilibrium" applies:

'Departures from local equilibrium are sufficiently small that all thermodynamic state quantities may be defined locally by the same relations as for systems at equilibrium'. Actually it may be shown that this assumption of local equilibrium follows from the assumption of a linear relation between the fluxes and driving forces (Truesdell, 1969).

With the help of this postulate, one is able to obtain an explicit expression for σ, the rate of entropy production per unit volume due to various irreversible processes taking place within the system. For isothermal, isobaric processes in the absence of external force fields, the rate of entropy production due to diffusion is given by

$$\sigma = -\frac{1}{T}\sum_{i=1}^{n} \mathbf{J}_i \cdot \nabla \mu_i = -\frac{1}{T}(\mathbf{J})^T \cdot (\nabla \mu) \geqq 0 \tag{23}$$

The second law of thermodynamics requires σ to be positive definite.

σ is seen to be a sum of scalar, or dot, products of two quantities; one of these is the diffusion flux and the other, the chemical potential gradient, may be interpreted as the "driving force" for diffusion. At equilibrium both the fluxes and the forces vanish simultaneously giving

$$\sigma = 0 \qquad | \text{ equilibrium } | \tag{24}$$

The chemical potential gradient arises in the theory of TIP as the proper driving force for diffusion. This is not surprising because the condition for diffusion equilibria is that the chemical potentials be equal in each phase and departures from equilibrium must be measured as deviations from such an equality.

We note that the n diffusion fluxes in (23) are not all independent due to the constraint (8). Further, at constant temperature (T) and pressure (p), the chemical potential gradients are related by the Gibbs-Duhem equation

$$\sum_{i=1}^{n} x_i \nabla \mu_i = 0 \tag{25}$$

Equations (8) and (25) may be used to write σ in terms of independent fluxes $\mathbf{J}_i$ and independent modified driving forces $\mathbf{Y}_i$ as

$$\sigma = \sum_{i=1}^{n-1} \mathbf{J}_i \cdot \mathbf{Y}_i \equiv (\mathbf{J})^T \cdot (\mathbf{Y}) \geqq 0 \tag{26}$$

where the $n-1$ independent modified driving forces $\mathbf{Y}_i$ are given by

$$\mathbf{Y}_i = -\sum_{k=1}^{n-1} A_{ik} \nabla \mu_k / T, \qquad i = 1,2,\ldots n-1 \tag{27}$$

The linear transformation coefficients A_{ik} are found to be

$$A_{ik} = \delta_{ik} + x_k / x_n, \qquad i,k = 1,2,\ldots n-1 \tag{28}$$

The simplest and entirely adequate constitutive relation between these independent fluxes $\mathbf{J}_i$ and driving forces $\mathbf{Y}_i$ is

$$(\mathbf{J}) = [L](\mathbf{Y}) \tag{29}$$

The transport coefficients L_{ik} $(i,k = 1,2,\ldots n-1)$ are called phenomenological or Onsager coefficients; they may be considered 'fundamental' inasmuch as they use driving forces arising from a fundamental thermodynamic theory. The second law of thermodynamics places some restrictions on the values these Onsager coefficients may take; these restrictions are derived below.

Combination of equations (26) and (29) gives

$$\sigma = (\mathbf{Y})^T [L] \cdot (\mathbf{Y}) \geqq 0 \tag{30}$$

Now the matrix of phenomenological coefficients may be split into its symmetric and anti-symmetric parts, i.e.

$$[L] = [L]_s + [L]_a \tag{31}$$

Substitution of equation (31) into equation (30) and use of the property that a positive definite quadratic with an anti-symmetric matrix of coefficients vanishes indentically gives (De Groot and Mazur, 1962)

$$\sigma = (\mathbf{Y})^T [L]_s \cdot (\mathbf{Y}) \geqq 0 \tag{32}$$

The anti-symmetric part of the matrix $[L]$ does not contribute to the rate of entropy production due to diffusion.

A sufficient condition for the entropy production rate σ to be positive definite is that the determinant of the symmetrized matrix of coefficients, $[L]_s$, be positive definite which requires that

$$\det |L_s| \geqq 0 \tag{33}$$

and that the principal cofactors be all positive. This implies that the diagonal elements are all positive

$$L_{ii} \geqq 0, \qquad i = 1,2,\ldots n-1 \tag{34}$$

whereas the off-diagonal elements must satisfy conditions of the form

$$L_{ii} L_{kk} - \tfrac{1}{4}(L_{ik} + L_{ki})^2 \geqq 0, \qquad i,k = 1,2,\ldots n-1 \tag{35}$$

and so on.

For a three-component system, for example, the restrictions on the Onsager coefficients are (Kirkaldy, 1970):

$$L_{11} \geqq 0;\ L_{22} \geqq 0;\ L_{11} L_{22} - \tfrac{1}{4}(L_{12} + L_{21})^2 \geqq 0 \tag{36}$$

This much information is obtained from TIP theory from only two postulates: local equilibrium and linear constitutive relations. Another assumption of TIP is that the matrix $[L]$ is symmetric, i.e.

$$[L] = [L]^T;\ [L]_a \equiv [0] \tag{37}$$

Equation (37) expresses the Onsager Reciprocal Relations (ORR), which may be looked upon as the third postulate of TIP, for postulates they are, subject to experimental confirmation or disproof.

The ORR have been the subject of many journal papers receiving support and also criticism, notably from Coleman and Truesdell (1960) and Truesdell (1969). All the available experimental evidence in multicomponent diffusion and other phenomena seem to verify the ORR and such verifications are continuing to appear in the literature. Miller (1960, 1969, 1974) has conveniently summarized the experimental evidence in support of the ORR, which appear to be generally valid for coupled transport processes.

From an engineer's view point, the ORR represent a saving in experimental labour, as they reduce the number of coefficients to be determined from $(n-1)^2$ to $n(n-1)/2$. For a ternary mixture the reduction is from 4 to 3; for a quaternary mixture the reduction is from 9 to 6 etc. Alternatively, if all the transport coefficients are determined, the ORR may be used as a consistency test on the experimental data.

The chemical potentials are not directly accessible by measurement and therefore before one may apply the ORR or any of the other second law restrictions, it is important to be able to relate the L_{ik} coefficients to the measurable D_{ik} coefficients. To do so we proceed as follows (De Groot and Mazur, 1962).

Under isothermal, isobaric conditions, the chemical potential gradients may be expressed in terms of the composition gradients as

$$\nabla \mu_i = \sum_{k=1}^{n-1} \frac{\partial \mu_i}{\partial x_k} \nabla x_k, \qquad i = 1,2,\ldots n-1 \tag{38}$$

The matrix of chemical potential–composition derivatives $[\partial\mu/\partial x]$ may be further expressed in terms of the activity coefficients, γ_i, in the mixture as follows:

$$\frac{\partial \mu_i}{\partial x_j} = RT\frac{\partial \ln \gamma_i x_i}{\partial x_j} = RT\left[\frac{\partial \ln x_i}{\partial x_j} + \frac{\partial \ln \gamma_i}{\partial x_j}\right] = \frac{RT}{x_i}\left[\delta_{ij} + \frac{x_i}{x_j}\frac{\partial \ln \gamma_i}{\partial \ln x_j}\right] = \frac{RT}{x_i}\Gamma_{ij}, \qquad i,j = 1,2\ldots n-1 \tag{39}$$

where we have defined a matrix of thermodynamic factors, $[\Gamma]$, with elements given by

$$\Gamma_{ij} = \delta_{ij} + \frac{x_i}{x_j}\frac{\partial \ln \gamma_i}{\partial \ln x_j}, \qquad i,j = 1,2,\ldots n-1 \tag{40}$$

We may therefore re-write equation (38) in the form

$$\nabla \mu_i = \frac{RT}{x_i}\sum_{k=1}^{n-1} \Gamma_{ik} \nabla x_k, \qquad i = 1,2,\ldots n-1 \tag{41}$$

or more compactly in matrix notation as

$$(\nabla \mu) = RT \ulcorner \frac{1}{x} \lrcorner [\Gamma] (\nabla x) \tag{42}$$

where $\ulcorner \frac{1}{x} \lrcorner$ represents a diagonal matrix with elements $\frac{1}{x_1}, \frac{1}{x_2}, \ldots \frac{1}{x_{n-1}}$.

Combination of equations (27), (29), (38) and (42) gives

$$
\begin{aligned}
(\mathbf{J}) &= -[L]\,[A]\,[\partial\mu/\partial x]\,(\nabla x)/T \\
&= -R\,[L]\,[A]\ulcorner\frac{1}{x}\lrcorner\,[\Gamma]\,(\nabla x)
\end{aligned}
\tag{43}
$$

Comparison of equations (22) and (43) shows the inter-relationship between the matrix of Fick's law diffusion coefficients and the matrix of Onsager coefficients,

$$
c\,[D] = \frac{1}{T}\,[L]\,[A]\,[\partial\mu/\partial x] = R\,[L]\,[A]\ulcorner\frac{1}{x}\lrcorner\,[\Gamma]
\tag{44}
$$

The symmetry requirement for the $[L]$ matrix may therefore be translated into restrictions on the coefficients D_{ik} (Kirkaldy, 1970; Yao, 1966). It is important to note that the matrix $[D]$ will not in general be symmetric. Application of the ORR therefore reduces the number of independent elements D_{ik} from $(n-1)$ to $n(n-1)/2$.

Now from thermodynamic stability considerations it can be shown that the determinant of the matrix $[\partial\mu/\partial x]$ is positive definite (Haase, 1969). The determinant of the linear transformation matrix $[A]$ may also be verified as being positive definite (cf. equation (28)). The determinant of the matrix of Onsager coefficients is positive definite from the second law requirement (cf. equations (33) and (37)). It can be seen from equation (44) that the matrix $[D]$ is the product of three matrices whose determinants are all positive definite. It follows directly from matrix theory that the eigenvalues of $[D]$ must be real and positive (Kirkaldy, 1970); the eigenvalues of $[D]$ being the roots of the determinantal equation

$$
\det\left|\,[D] - \hat{D}\ulcorner I\lrcorner\,\right| = 0
\tag{45}
$$

For an n-component system, equation (45) reduces to an $n-1$ th order polynomial in $\hat{D}$, giving $n-1$ eigenvalues: $\hat{D}_1, \hat{D}_2, \ldots \hat{D}_{n-1}$. For a ternary system, the two roots $\hat{D}_1$ and $\hat{D}_2$ can be found explicitly from

$$
\hat{D}_{1,2} = \frac{(D_{11} + D_{22}) \pm (D_{11} - D_{22})\sqrt{1 + 4\,D_{12}D_{21}/(D_{11} - D_{22})^2}}{2}
\tag{46}
$$

The condition for real and positive eigenvalues $\hat{D}_1$ and $\hat{D}_2$ for a ternary system can therefore be expressed as (Kirkaldy, 1970; Yao, 1966):

$$
D_{11} + D_{22} > 0 \tag{47}
$$

$$
D_{11}D_{22} - D_{12}D_{21} > 0 \tag{48}
$$

$$
(D_{11} - D_{22})^2 + 4\,D_{12}D_{21} > 0 \tag{49}
$$

It is interesting to note that thermodynamic stability considerations do not require the diagonal elements D_{11} and D_{22} to be individually positive. If recourse is made to the kinetic theory of gases, it can be shown that the main coefficients are individually positive, i.e.

$$D_{11} > 0; D_{22} > 0 \tag{50}$$

All available information on experimental measurements on D_{ik} suggests the general validity of requirement (50).

The cross coefficients D_{ik} $(i \neq k)$ can be of either sign; indeed it is possible to alter the sign of these cross-coefficients by altering the numbering of the components.

The theory of TIP therefore provides some very useful information on the structure of the matrix of practical diffusion coefficients $[D]$.

II. 1.c Generalized Maxwell-Stefan Formulation for Diffusion

In the Onsager formulation of the constitutive relations, the diffusion fluxes are related to the chemical potential gradients by linear relations (29). As an alternative to this formulation, the chemical potential gradients may be written as linear functions of the diffusion fluxes, or equivalently the diffusion velocities, as (see Standart, Taylor, and Krishna, 1979 for derivation)

$$\frac{1}{RT} \nabla \mu_i = \sum_{\substack{k=1 \\ k \neq 1}}^{n} \frac{x_k (\mathbf{u}_k - \mathbf{u}_i)}{Ð_{ik}} \qquad i = 1,2,\ldots n \tag{51}$$

which is the generalized Maxwell-Stefan formulation of the constitutive relations for n-component diffusion (Lightfoot, Cussler and Rettig, 1962; Slattery, 1972). The coefficients $Ð_{ik}$ are the generalized Maxwell-Stefan diffusion coefficients and these coefficients exhibit the symmetry property (Truesdell, 1969)

$$Ð_{ik} = Ð_{ki} \qquad \begin{matrix} i,k = 1,2,\ldots n \\ i \neq k \end{matrix} \tag{52}$$

equivalent to the ORR. There are therefore $n\,(n-1)/2$ of these coefficients characterizing multicomponent diffusion. The $Ð_{ii}$ are undefined.

If we multiply both sides of equations (51) by x_i we may rewrite the generalized Maxwell-Stefan equations, in view of equations (3)–(7), as

$$\frac{1}{RT} x_i \nabla \mu_i = \sum_{\substack{k=1 \\ k \neq 1}}^{n} \frac{x_i \mathbf{N}_k - x_k \mathbf{N}_i}{c\, Ð_{ik}} = \sum_{\substack{k=1 \\ k \neq 1}}^{n} \frac{x_i \mathbf{J}_k - x_k \mathbf{J}_i}{c\, Ð_{ik}} \quad , \quad i = 1,2,\ldots n-1 \tag{53}$$

where only $n-1$ equations are written because of the restriction (25).

If we define a matrix $[B]$ with elements given by

$$B_{ii} = \frac{x_i}{\text{Đ}_{in}} + \sum_{\substack{k=1\\k\neq i}}^{n} \frac{x_k}{\text{Đ}_{ik}}, \qquad i = 1,2,\ldots n-1 \tag{54}$$

$$B_{ij} = -\,x_i \left[\frac{1}{\text{Đ}_{ij}} - \frac{1}{\text{Đ}_{in}}\right], \qquad \begin{matrix} i,j = 1,2,\ldots n-1 \\ i\neq j \end{matrix} \tag{55}$$

we may rewrite equations (53) in a compact matrix notation, in view of equations (8) and (42), as

$$c\,[\Gamma]\,(\,\nabla x) = -\,[B]\,(\mathbf{J}) \tag{56}$$

where all matrices are of dimension $n-1$.

Comparison of equation (56) with (43) gives the inter-relationship between the matrix of Onsager coefficients $[L]$ and the generalized Maxwell-Stefan diffusion coefficients. Thus we have

$$[L] = \frac{c}{R}\,[B]^{-1} \left\lceil \frac{1}{x} \right\rfloor^{-1} [A]^{-1} = \frac{c}{R}\,\{[A] \left\lceil \frac{1}{x} \right\rfloor [B]\}^{-1} \tag{57}$$

It may be easily verified by use of relation (57) that the symmetry requirement for the generalized Maxwell-Stefan diffusion coefficients, equation (52), is consistent with the ORR, equation (37).

Unlike the Fickian D_{ik}, the values of the Maxwell-Stefan diffusion coefficients Đ_{ik} do not depend on the arbitrary labelling of the nth component. The coefficient Đ_{ik} essentially reflects the i-k pair collision phenomena and may be closely related to the molecular processes within the fluid phase. For mixtures of ideal gases, the Maxwell-Stefan diffusion coefficients Đ_{ik} reduce to the binary molecular diffusion coefficient $\mathscr{D}_{yik}$ in the gas phase, i.e.

$$\text{Đ}_{ik} = \mathscr{D}_{yik}, \qquad \begin{matrix} i,k = 1,2,\ldots n \\ i\neq k \end{matrix} \tag{58}$$

For ideal gas mixtures the $\mathscr{D}_{yik}$ are esentially composition independent and the generalized Maxwell-Stefan diffusion equations (53) simplify to

$$\nabla\, y_i = \sum_{\substack{k=1\\k\neq i}}^{n} \frac{y_i\mathbf{N}_k - y_k\mathbf{N}_i}{c\;\mathscr{D}_{yik}} = \sum_{\substack{k=1\\k\neq i}}^{n} \frac{y_i\mathbf{J}_k - y_k\mathbf{J}_i}{c\;\mathscr{D}_{yik}}, \qquad i = 1,2,\ldots n-1 \tag{59}$$

where we use y_i to denote gas phase mole fractions; the matrix of thermodynamic factors reduces to the identity matrix for ideal fluid mixtures. Equations (59) may also be written equivalently in $n-1$ dimensional matrix notation as (cf. equation (56))

$$c\,(\,\nabla\, y) = -\,[B]\,(\mathbf{J}) \tag{60}$$

where the elements of the matrix $[B]$ are given by equations (54) and (55) with the binary duffusion coefficient $\mathscr{D}_{ik}$ replacing D_{ik} and the mole fractions y_i replacing x_i.

For non-ideal liquid mixtures the D_{ik} cannot normally be identified with the diffusion coefficient of the binary pair $\mathscr{D}_{xik}$. Both the D_{ik} and the $\mathscr{D}_{xik}$ are functions of composition in addition to being dependent on temperature. The variation of the D_{ik} with composition is theoretically predictable for a binary system (Vignes, 1966) and may be estimated from the infinite dilution values. The prediction of the D_{ik} for a multicomponent system is a subject of current research interest (Cullinan, 1966–1975; Cussler, 1976).

Since the Maxwell-Stefan diffusion coefficients D_{ik} are amenable to simple molecular interpretation and theoretical prediction, the generalized Maxwell-Stefan equations (53), (56) are indeed convenient formulations. Further, comparison of equation (56) with (22) shows

$$[D] = [B]^{-1}\,[\Gamma] \tag{61}$$

which provides a general method for predicting the elements of the Fick's law diffusion coefficients.

For ideal gas mixtures, equation (61) simplifies to

$$[D_y] = [B]^{-1} \tag{62}$$

and therefore the elements D_{yik} can be estimated from information on the diffusion coefficients of the binary pairs, $\mathscr{D}_{yik}$. For a ternary system, the matrix inversion in (62) can be carried out explicitly and the four elements of the matrix $[D_y]$ are obtained as

$$D_{y11} = \mathscr{D}_{y13}\,(y_1\ \mathscr{D}_{y23} + (1-y_1)\ \mathscr{D}_{y12})/S \tag{63}$$

$$D_{y12} = y_1\ \mathscr{D}_{y23}\,(\mathscr{D}_{y13} - \mathscr{D}_{y12})/S \tag{64}$$

$$D_{y21} = y_2\ \mathscr{D}_{y13}\,(\mathscr{D}_{y23} - \mathscr{D}_{y12})S \tag{65}$$

$$D_{y22} = \mathscr{D}_{y23}\,(y_2\ \mathscr{D}_{y13} + (1-y_2)\ \mathscr{D}_{y12})/S \qquad (67)$$

where

$$S = y_1\ \mathscr{D}_{y23} + y_2\ \mathscr{D}_{y13} + y_3\ \mathscr{D}_{y12} \qquad (67)$$

The diffusion coefficients of the binary pairs $\mathscr{D}_{yik}$ can be estimated from the kinetic theory of gases (Chapman and Cowling, 1970; Hirschfelder, Curtis and Bird, 1954) to a reasonable degree of accuracy particularly for non-polar molecules. The matrix of diffusion coefficients may therefore be calculated using (62). It may be verified from equations (63)–(67) that if $\mathscr{D}_{y12} = \mathscr{D}_{y13} = \mathscr{D}_{y23} = \mathscr{D}_y$, then the matrix of diffusion coefficients degenerates to a scalar times the identity matrix, i.e.

$$[D_y] = \mathscr{D}_y \ \lceil I \rfloor \qquad |\text{special}| \tag{68}$$

It is interesting now to compare the above result (68) with (20) and the discussions following it.

For liquid mixtures, the calculation of the elements D_{xik} from (61) requires complete information on the Maxwell-Stefan diffusivities $Ð_{ik}$ and the activity coefficients γ_i in solution. Since the prediction methods for the $Ð_{ik}$ are still under development, experimental measurements of the matrix $[D_x]$ are necessary in most cases. Measurement techniques are discussed by Cussler (1976) and Dunlop *et al* (1972).

III. SOLUTION TO PROBLEMS IN ISOTHERMAL MULTICOMPONENT DIFFUSION

The solution to a problem involving diffusion, under isothermal conditions, in an n-component mixture consists in solving the differential equations of continuity (11) together with the appropriate constitutive relations for the diffusion fluxes J_i, discussed in the previous section. The method of solution to be used in each case depends on whether the diffusion occurs in the gaseous or liquid phase, whether the diffusion can be considered uni-dimensional or not and whether or not steady-state, or at least quasi steady-state conditions hold. This is because for certain simplified situations, exact analytic solutions for the composition profiles and fluxes are possible. We first consider the problem of steady-state one dimensional diffusion in mixtures of ideal gases at constant temperature and total pressure.

III.1. Steady-State Unidimensional Diffusion in Ideal Gas Mixtures

Consider diffusion in an ideal gas mixture with n components. Under essentially isothermal, isobaric conditions, the total molar density of the gas mixture c may be considered constant. Let us further assume that diffusion takes place under steady-state conditions and that the compositions at either end of the diffusion path, z, are known and independent of time. Thus we have the boundary conditions:

$$\begin{aligned} &\text{at } z = 0,\ y_i = y_{i0}, \qquad i = 1,2,\dots n \\ &\text{at } z = \delta,\ y_i = y_{i\delta}, \end{aligned} \tag{69}$$

Now, for steady-state unidimensional diffusion, the equations of continuity (9) simplify to

$$\frac{dN_i}{dz} = 0, \qquad i = 1,2,\dots n \tag{70}$$

The equation of continuity for the total mixture (10) also simplifies to

$$\frac{dN_t}{dz} = 0$$

Thus the constituent and mixture total fluxes N_i and N_t are z-invariant. From a practical point of view it is important to determine the total fluxes N_i, given compositions at either end of the diffusion path, equation (69). There are n total fluxes N_i to determine, for the mixture total flux N_t is then simply given by equation (4).

Now, for ideal gas mixtures the most convenient representation of the constitutive equations is the Maxwell-Stefan formulation (59). There are only $n-1$ of these relations which are independent. Clearly the determination of n fluxes N_i requires a further relationship. This relationship—termed the 'determinancy condition'—may be written in the general format:

$$\sum_{i=1}^{n} \nu_i N_i = 0 \tag{72}$$

For example if conditions of equimolar counter-diffusion are specified, then we have

$$\nu_i = 1, \qquad i = 1,2,\ldots n \tag{73}$$

On the other hand if we have diffusion of $n-1$ species through a stagnant (inert) nth component, then

$$N_n = 0 \tag{74}$$

and therefore the parameters ν_i in (72) are given as

$$\nu_i = 0, \qquad i = 1,2,\ldots n-1 \tag{75}$$

and

$$\nu_n = 1 \tag{76}$$

In problems involving diffusion with heterogeneous catalytic reactions, the parameters ν_i are determined by the stoichiometry of the reaction. The determinancy condition in most practical cases may therefore be written in the form (72).

In proceeding with the solution of the $n-1$ equations (59) subject to (72), it is convenient to define a dimensionless distance along the diffusion path:

$$\eta \equiv z/\delta \tag{77}$$

and 'transfer' coefficients', $\boldsymbol{k}_{ik}$, of the binary pairs i–k as

$$\boldsymbol{k}_{ik} = c\,\mathcal{D}_{yik}/\delta\,, \qquad \begin{matrix} i,k = 1,2,\ldots n \\ i \neq k \end{matrix} \tag{78}$$

With these definitions the equations (59) may be written as

$$\frac{dy_i}{d\eta} = \sum_{\substack{k=1 \\ k\neq i}}^{n} \frac{y_i N_k - y_k N_i}{\boldsymbol{k}_{ik}} = \sum_{\substack{k=1 \\ k\neq i}}^{n} \frac{y_i J_k - y_k J_i}{\boldsymbol{k}_{ik}}\,, \qquad i = 1,2,\ldots n-1 \tag{79}$$

We therefore seek a solution for the n total fluxes N_i from equations (79) and (72), with the boundary conditions

$$\begin{aligned} &\text{at } \eta = 0, y_i = y_{i0}, \\ & \qquad\qquad\qquad\qquad i = 1,2,\ldots n \\ &\text{at } \eta = 1, y_i = y_{i\delta}, \end{aligned} \tag{80}$$

For ideal gas mixtures the binary diffusion coefficients $\mathscr{D}_{yik}$ are virtually composition independent and therefore the mass transfer coefficients k_{ik} in (79) are independent of the parameter η. The diffusion fluxes J_i vary along the diffusion path even though the N_i are η-invariant.

For a two-component system, the composition profiles are obtained as (BSL)

$$y_1 - y_{10} = \frac{e^{\phi\eta} - 1}{e^{\phi} - 1}(y_{1\delta} - y_{10}) \tag{81}$$

with the diffusion flux of component 1 given by

$$J_{10} = k_{12}\frac{\phi}{e^{\phi} - 1}(y_{10} - y_{1\delta}) \tag{82}$$

The diffusion flux of component 2 is simply (cf. equation (8))

$$J_{20} = -J_{10} \tag{83}$$

The factor ϕ in equations (81) and (82) is a dimensionless mass transfer rate factor (BSL) given as

$$\phi \equiv (N_1 + N_2)/\, k_{12} \tag{84}$$

For equimolar counter-diffusion in the binary systems, $N_t = 0$, and we have

$$N_1 = J_{10} = J_{1\delta} = k_{12}(y_{10} - y_{1\delta}) \tag{85}$$

and for diffusion of species 1 through stagnant 2 ($N_2 = 0$), we have the total flux of 1 given by

$$N_1 = \frac{J_{10}}{1 - y_{10}} = k_{12}\left(\frac{\phi}{e^{\phi} - 1}\right)\frac{(y_{10} - y_{1\delta})}{(1 - y_{10})} \tag{86}$$

which is more usually written as

$$N_1 = k_{12}\ln\frac{1 - y_{1\delta}}{1 - y_{10}} \tag{87}$$

Analytic solutions to (79) for the three-component case for various determinancy conditions are available in the literature (Benedict and Boas, 1951; Cichelli *et al*, 1951; Gilliland, 1937; Hsu and Bird, 1960; Johns and De Gance, 1975; Keyes and Pigford, 1957; Toor, 1957). Krishna and Standart (1976b) obtained a general solution to the n-component case using matrix analysis. Their results are of general applicability and presented in convenient form. We follow their development below.

The following parameters are defined:

(i) a matrix $[\Phi]$ of dimensionless mass transfer rate factors with elements given by

$$\Phi_{ii} = \frac{N_i}{k_{in}} + \sum_{\substack{k=1\\k\neq i}}^{n} \frac{N_k}{k_{ik}}, \qquad i = 1,2,\ldots n-1 \tag{88}$$

$$\Phi_{ij} = -N_i\left[\frac{1}{k_{ij}} - \frac{1}{k_{in}}\right], \qquad \begin{matrix} i,j = 1,2,\ldots n-1 \\ i\neq j \end{matrix} \tag{89}$$

(ii) a column matrix (ξ) with elements

$$\xi_i = -N_i/k_{in}, \qquad i = 1,2,\ldots n-1 \tag{90}$$

(iii) a square matrix $[\mathscr{B}_0]$ with elements given by

$$\mathscr{B}_{0ii} = \frac{y_{i0}}{k_{in}} + \sum_{\substack{k=1\\k\neq i}}^{n} \frac{y_{k0}}{k_{ik}}, \qquad i = 1,2,\ldots n-1 \tag{91}$$

$$\mathscr{B}_{0ij} = -y_{i0}\left[\frac{1}{k_{ij}} - \frac{1}{k_{in}}\right], \qquad \begin{matrix} i = 1,2,\ldots n-1 \\ i\neq j \end{matrix} \tag{92}$$

With above definitions, the equations (79) may be written in $n-1$ dimensional matrix notation as

$$\frac{d(y)}{d\eta} = [\Phi]\,(y) + (\xi) \tag{93}$$

with the diffusion fluxes J_{i0} given by (cf. equation (60))

$$(J_0) = -[\mathscr{B}_0]^{-1} \left.\frac{d(y)}{d\eta}\right|_{\eta=0} \tag{94}$$

Basically the solution procedure consists in solving (93) to obtain the composition profiles which may be used to evaluate the composition gradient at $\eta = 0$ and then combined with (94) to yield the diffusion fluxes J_{i0}.

The solution of the linear matrix differential equation (93) with the boundary conditions (80) is straightforward (Amundson, 1966; Krishna and Standart, 1976b) and yields the composition profiles in $n-1$ dimensional matrix notation as

$$(y-y_0)=\{\exp[\Phi]\eta-\ulcorner I\lrcorner\}\{\exp[\Phi]-\ulcorner I\lrcorner\}^{-1}(y_\delta-y_0)\tag{95}$$

which is seen to be the exact matrix analogue of equation (81). The composition gradient at the position $\eta=0$ can be obtained as

$$\frac{d(y)}{d\eta}\bigg|_{\eta=0}=[\Phi]\{\exp[\Phi]-\ulcorner I\lrcorner\}^{-1}(y_\delta-y_0)\tag{96}$$

and therefore the diffusion fluxes J_{i0} can be expressed in view of equation (94) as

$$(J_0)=[\mathscr{B}_0]^{-1}[\Phi]\{\exp[\Phi]-\ulcorner I\lrcorner\}^{-1}(y_0-y_\delta)\tag{97}$$

It is convenient to define a matrix of 'mass transfer coefficients', $[k_0^\bullet]$, by

$$(J_0)=[k_0^\bullet](y_0-y_\delta)\tag{98}$$

so that

$$[k_0^\bullet]=[\mathscr{B}_0]^{-1}[\Xi]\tag{99}$$

where we further define a matrix of correction factors

$$[\Xi]\equiv[\Phi]\{\exp[\Phi]-\ulcorner I\lrcorner\}^{-1}\tag{100}$$

The mass transfer coefficients defined in (98) are functions of the total rates of transfer N_i; we emphasize this fact by using a superscript black dot on the transfer coefficients $k^\bullet_{0ij}$. The definitive discussion of transfer processes at high mass transfer rates for binary systems is given in BSL. The above relations represent the extension to the general n-component case.

It may be verified from equations (88), (89) and (100) that for vanishing rates of transfer ($N_i \rightarrow 0$), the matrix of correction factors $[\Xi]$ reduces to the identity matrix and when this happens the matrix of 'finite flux' mass transfer coefficients $[k_0^\bullet]$ reduces to $[\mathscr{B}_0]^{-1}$, which may therefore be defined as the matrix of 'zero flux' mass transfer coefficients. Thus taking

$$[k_0]=[\mathscr{B}_0]^{-1}\tag{101}$$

allows calculation of the matrix of 'zero flux' transfer coefficients.

The formal calculation of the total fluxes N_i from a knowledge of the diffusion fluxes J_{i0} may be carried out as follows. We multiply equations (7) by ν_i and sum over the n species to obtain, in view of (8) and (72),

$$N_t = -\frac{\sum_{k=1}^{n-1}(\nu_k - \nu_n)J_{k0}}{\sum_{k=1}^{n} \nu_k y_{k0}} \tag{102}$$

and therefore $n-1$ total fluxes N_i may be obtained from the $n-1$ diffusion fluxes J_{i0} from the relation

$$N_i = \sum_{i=1}^{n-1} (\delta_{ik} - y_{i0}\Lambda_k) J_{k0}, \qquad i = 1,2,\ldots n-1 \tag{103}$$

with the nth flux N_n determined from (cf. equation (72))

$$N_n = -\sum_{k=1}^{n-1} \frac{\nu_i}{\nu_n} N_i \tag{104}$$

The parameters Λ_k in (103) are given by (cf. equation (102))

$$\Lambda_k = (\nu_k - \nu_n)/\{\sum_{i=1}^{n} \nu_i y_{i0}\} \qquad k = 1,2,\ldots n-1 \tag{105}$$

Equations (98), (103) and (104) represent the formal solution to the problem under consideration. The calculation of the total fluxes N_i is not truly explicit and involves a trial and error procedure. Convergence is assured if the following iteration procedure is adopted (Krishna and Standart, 1976b):

STEP I Calculate the matrix of zero flux mass transfer coefficients, $[k_0]$, from (91), (92) and (101),

STEP II Assume for the first iteration that the matrix of correction factors $[\Xi]$ is given by the identity matrix. Calculate the first approximation to the matrix of 'finite flux' mass transfer coefficients $[k_0^\bullet]$, from (99).

STEP III Determine the diffusion fluxes J_{i0} from (98) and calculate the n total fluxes N_i from equations (103)–(105),

STEP IV With this estimate of the fluxes N_i, obtain the elements of $[\Phi]$ and calculate the elements of the matrix of correction factors from (100). The determination of $[\Xi]$ requires the use of Sylvester's theorem (Amundson, 1966). Explicit expressions for $[\Xi]$ for the ternary mixture for the equimolar counter diffusion case (73) and the stagnant nth component case (74) are given by Krishna and Standart (1976b).

STEP V With the new estimate of the matrix $[\Xi]$ the 'finite flux' coefficients $[k_0^\bullet]$ may be reevaluated and the steps III–V repeated till convergence is obtained on each individual N_i.

The steady-state analysis considered above forms the basis of the 'film' model for the estimation of multicomponent mass transfer coefficients.

III.2. Steady-State Unidimensional Diffusion in Non-Ideal Liquid Mixtures

For non-ideal liquid mixtures the generalized Maxwell-Stefan diffusion coefficients $Đ_{ik}$ are not independent of composition. Further, there is a complication due to the thermodynamic non-ideality of the mixture, reflected by the elements of the matrix of thermodynamic factors $[\Gamma]$. Strictly speaking, therefore, a general analytic solution for steady-state diffusion in liquid mixtures is not possible. Krishna (1976a) has suggested the following extension of the ideal gas phase analysis to liquid mixtures.

(i) Obtain suitably averaged values of the generalized Maxwell-Stefan diffusion coefficients $Đ_{ik}$ over the range of compositions x_{i0} to $x_{i\delta}$.

(ii) Calculate transfer coefficients $\mathscr{k}_{ik}$ from

$$\mathscr{k}_{ik} = (c\, Đ_{ik})_{\mathrm{av}}/\delta, \qquad i,k = 1,2,\ldots n \tag{106}$$

(iii) The elements of $[\mathscr{B}_0]$ are estimated using equations (91) and (92) using x_{i0} in place of the gas phase mole fractions y_{i0}.

(iv) The elements of the matrix of thermodynamic factors $[\Gamma]$ are calculated from equation (40) at a suitable mean composition between x_{i0} and $x_{i\delta}$.

(v) The matrix of 'zero flux' mass transfer coefficients $[k_0]$ is obtained from

$$[k_0] = [\mathscr{B}_0]^{-1}\,[\Gamma] \tag{107}$$

(vi) A modified matrix of dimensionless rate factors $[\Theta]$ is defined as

$$[\Theta] \equiv [\Gamma]^{-1}\,[\Phi] \tag{108}$$

The diffusion fluxes J_{i0} are then obtained from the equation (98) with the matrix of 'finite flux' mass transfer coefficients, $[k_0^{\bullet}]$, given by

$$[k_0^{\bullet}] = [k_0]\,[\Theta]\,\{\exp\,[\Theta] - [I]\}^{-1} \tag{109}$$

The calculation of the total fluxes N_i is then carried out exactly as for the ideal gas case considered earlier.

For further applications of the above matrix methods of solution to the Maxwell-Stefan equations, see Krishna (1976a,e,f; 1977a).

III.3 General Method of Solution to Multicomponent Diffusion. Linearized Theory of Toor (1964) and Stewart and Prober (1964)

On introducing the generalized Fick's law formulation (21) into the continuity relations (11) we obtain $n-1$ independent differential equations

$$c\,\frac{dx_i}{dt} = \nabla \cdot \left[c \sum_{k=1}^{n-1} D_{ik} \nabla x_k\right], \qquad i = 1,2,\ldots n-1 \tag{110}$$

Equations (110) represent a set of $n-1$ coupled partial differential equations; the coupling arises due to the presence of the cross coefficients D_{ik} $(i \neq k)$ in the matrix of practical diffusion coefficients. The elements of the matrix $[D]$ are dependent on composition. For ideal gas mixtures, they are calculable with the aid of the Maxwell-Stefan equations (cf. equation (62)) from the binary diffusion coefficients $\mathcal{D}_{yik}$. For the general case of non-ideal fluid mixtures the elements of $[D]$ have to be evaluated experimentally; as discussed earlier prediction methods for $[D_x]$ are still under development.

Toor (1964) and Stewart and Prober (1964) independently put forward a general method of solution to equations (110) which essentially consists in assuming that $c\ [D]$ can be considered a constant matrix in the diffusion process. With this assumption equations (110) reduce to

$$\frac{dx_i}{dt} = \sum_{k=1}^{n-1} D_{ik} \nabla^2 x_k, \qquad i = 1,2,\ldots n-1 \tag{111}$$

which can be represented conveniently in $n-1$ dimensional matrix notation as

$$\frac{d(x)}{dt} \equiv \frac{\partial(x)}{\partial t} + \mathbf{u} \cdot (\nabla x) = [D] \nabla^2 (x) \tag{112}$$

The matrix differential equation (112) can be uncoupled by a similarity transformation (Amundson, 1966; Toor, 1964). The uncoupling procedure is as follows.

For the matrix of coefficients $[D]$, a modal matrix $[P]$ can be found such that

$$[P]^{-1} [D] [P] = \begin{bmatrix} \hat{D}_1 & & & \\ & \hat{D}_2 & & \\ & & \ddots & \\ & & & \hat{D}_{n-1} \end{bmatrix} \equiv \ulcorner \hat{D} \lrcorner \tag{113}$$

where $\hat{D}_1, \hat{D}_2, \ldots \hat{D}_{n-1}$ are the eigenvalues of the matrix $[D]$. The requirement of the second law of thermodynamics, $\sigma \geqq 0$, ensures that the $\hat{D}_i$ are all real and positive numbers and form a complete set even if there are repeated roots (Cullinan, 1965).

On premultiplying equation (112) by $[P]^{-1}$ we obtain

$$\frac{\partial(\hat{x})}{\partial t} + \mathbf{u} \cdot \nabla (\hat{x}) = \ulcorner \hat{D} \lrcorner \ \nabla^2 (\hat{x}) \tag{114}$$

where we define pseudo-compositions, $\hat{x}_i$, by

$$(\hat{x}) \equiv [P]^{-1} (x) \tag{115}$$

Equation (22) may also be premultiplied by $[P]^{-1}$ to yield

$$(\hat{\mathbf{J}}) \equiv -c \ulcorner \hat{D} \lrcorner \, (\nabla \hat{x}) \tag{116}$$

where the pseudo-diffusion fluxes $\hat{\mathbf{J}}_i$ are given by

$$(\hat{\mathbf{J}}) = [P]^{-1} (\mathbf{J}) \tag{117}$$

Examination of equations (114) and (116) shows that the similarity transformation reduces the original set of $n-1$ coupled differential equations (111) to a series of $n-1$ uncoupled equations (114) in pseudo-compositions,

$$\frac{\partial \hat{x}_i}{\partial t} + \mathbf{u} \cdot \nabla \hat{x}_i = \hat{D}_i \nabla^2 \hat{x}_i, \qquad i = 1,2,\ldots n-1 \tag{118}$$

with pseudo-diffusion fluxes given by a set of $n-1$ uncoupled constitutive relations

$$\hat{\mathbf{J}}_i = -c \hat{D}_i \nabla \hat{x}_i, \qquad i = 1,2,\ldots n-1 \tag{119}$$

The pseudo variables behave as though they were each the corresponding variables of a binary mixture with the diffusion coefficient $\hat{D}_i$. Therefore if the initial and boundary conditions can also be transformed to these pseudo compositions and fluxes by the same transformation and if free convection is not involved, the diagonalized equations represent a series of independent *binary* type problems, $n-1$ in number. If free or forced convection is involved, we must use the non-linear equation (118), where the molar average velocity $\mathbf{u}$ must be found from the solution giving the total mixture flux $\mathbf{N}_t$. The problem is relatively simple if mechanical equilibrium may be assumed. If however the equations of motion of the fluid must also be taken into account, the diffusion equations must be solved in terms of the *mass* average velocity and an iteration employed to find the molar average velocity (Stewart and Prober, 1964). Note that the (molar average) velocity $\mathbf{u}$ in equation (118) is not affected by the diagonalization transformation. Solutions to binary diffusion problems are available for a wide range of initial and boundary conditions (BSL; Crank, 1975) and therefore the solutions to each of the $n-1$ diffusion problems in pseudo-compositions can be written down straightaway. All such solutions would be in terms of pseudo-compositions and pseudo-fluxes. In order to recover the solution to the original problem in terms of real variables, it only remains to apply the inverse transformations:

$$(x) = [P] \, (\hat{x}) \tag{120}$$

and

$$(\mathbf{J}) = [P] \, (\hat{\mathbf{J}}) \tag{121}$$

The assumption of a constant matrix of diffusion coefficients therefore allows a host of solutions to multicomponent diffusion problems to be obtained quite simply; the theory of Toor and Stewart and Prober is also referred to as the linearized theory of multicomponent mass transfer because the set of non-linear differential equations (110) is linearized to give the set (111). One might expect the results of the linearized theory to be close to 'exact' solutions for small changes in concentration but the few experimental results which are available (Arnold and Toor, 1967) indicate that the errors caused by the assumption of constant c $[D]$ are not serious even for moderate changes in concentration.

The application of the linearized theory will be illustrated by considering a few typical diffusion problems.

III.4. EXAMPLES ILLUSTRATING THE LINEARIZED THEORY OF MULTICOMPONENT MASS TRANSFER

III.4. Restricted Diffusion in an Ideal Three-Component Gas Mixture

Here we consider the analysis of the well-known Loschmidt experiment for a three component gaseous system (Arnold and Toor, 1967). This example is of practical use in the measurement of multicomponent diffusion coefficients.

Two identical cylindrical compartments, each of length l, are filled with ternary gas mixtures of different compositions and joined end to end at time zero. Composition profiles for the diffusing species are to be determined; the measurement of such profiles may be used to calculate the elements of $[D_y]$.

At constant temperature and pressure inside the diffusion cell, the mixture density c remains constant and the molar average velocity u vanishes everywhere corresponding to the requirement of equimolar counter diffusion:

$$N_t = c\,u = 0 \tag{122}$$

Equation (112) therefore simplifies to

$$\frac{\partial(y)}{\partial t} = [D]\,\frac{\partial^2(y)}{\partial z^2} \tag{123}$$

with the initial and boundary conditions given by

$$\begin{aligned} &t \geqq 0, \quad 0 < z < l, \qquad (y) = (y^+) \\ &t \geqq 0, \ -l < z < 0, \qquad (y) = (y^-) \\ &t > 0, \quad z = \pm l, \quad \frac{\partial(y)}{\partial z} = 0 \end{aligned} \tag{124}$$

The first step in the application of the uncoupling of (123) is the diagonalization of the matrix $[D]$. For a ternary system the eigenvalues $\hat{D}_1$ and $\hat{D}_2$ are given by equation (46) and the modal matrix $[P]$ is found to be given by

$$[P] = \begin{bmatrix} 1 & \dfrac{D_{12}}{\hat{D}_2 - D_{11}} \\ \dfrac{\hat{D}_1 - D_{11}}{D_{12}} & 1 \end{bmatrix} \equiv \begin{bmatrix} 1 & \dfrac{\hat{D}_2 - D_{22}}{D_{21}} \\ \dfrac{D_{21}}{\hat{D}_1 - D_{22}} & 1 \end{bmatrix} \tag{125}$$

When D_{12} and D_{21} are negligibly small, $\hat{D}_1 \rightarrow D_{11}$ and $\hat{D}_2 \rightarrow D_{22}$. For this case the modal matrix $[P]$, and therefore $[P]^{-1}$, simplify to unit matrices and the equations (123) are not coupled. When this simplification does not hold, we must solve (123) by uncoupling them using the similarity transformation.

Multiplying (123) by $[P]^{-1}$ we transform the original problem into a set of two uncoupled equations

$$\frac{\partial \hat{y}_i}{\partial t} = \hat{D}_i \frac{\partial^2 \hat{y}_i}{\partial z^2}, \qquad i = 1,2 \tag{126}$$

The initial and boundary conditions are also transformed as

$$\begin{aligned} &t \leqq 0, \quad 0 < z < l, \quad \hat{y}_i = \hat{y}_i^+, \qquad i = 1,2 \\ &t \leqq 0, \quad -l < z < 0, \quad \hat{y}_i = \hat{y}_i^-, \qquad i = 1,2 \\ &t > 0, \quad z = \pm\, l, \quad \partial \hat{y}_i / \partial x = 0, \qquad i = 1,2 \end{aligned} \tag{127}$$

The solution to equations (126) subject to (127) may be written down straightforwardly as the solution to the corresponding binary diffusion problem is available (Arnold and Toor, 1967; Crank, 1975). Thus the pseudo composition profiles may be written as

$$\{\hat{y}_i - \hat{y}_i^-\} = \hat{f}_i(\hat{D}_i, t, z)\, \{\hat{y}_i^+ - \hat{y}_i^-\}, \qquad i = 1,2 \tag{128}$$

where the pseudo-functions $\hat{f}_i$ are given by

$$\hat{f}_i(\hat{D}_i, t, z) = \tfrac{1}{2} \left[1 \pm \frac{2}{\pi} \sum_{n=0}^{\infty} \left[\frac{1}{m} \sin \frac{m\pi z}{l} \exp \left\{ - \frac{m^2 \pi^2}{l^2} \hat{D}_i t \right\} \right] \right], \qquad i = 1,2 \tag{129}$$

with $m = n + \tfrac{1}{2}$.

Equation (128) in matrix notation is

$$(\hat{y} - \hat{y}^-) = \ulcorner \hat{f} \lrcorner \, (\hat{y}^+ - \hat{y}^-) \tag{130}$$

where $\ulcorner \hat{f} \lrcorner$ is a diagonal matrix with elements $\hat{f}_1$ and $\hat{f}_2$ given by (129).

To obtain the composition profiles in terms of the original variables in (123) we premultiply (130) by $[P]$ to obtain

$$(y - y^-) = [f]\,(y^+ - y^-) \tag{131}$$

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

$$[f] = [P] \ulcorner \hat{f} \lrcorner [P]^{-1} \tag{132}$$

Examination of equations (113) and (132) shows that the matrices $[f]$ and $[D]$ are closely related for they are diagonalized by the same similarity transformation, i.e. they have the same modal matrix $[P]$. $[f]$ may be evaluated in general by utilizing (132).

From equations (128)–(132) it is clear that the matrix $[f]$ is the same analytic function of $[D]$ as $\hat{f}_i$ *is of* $\hat{D}_i$, i.e.

$$[f] = f\{[D]\} \tag{133}$$

Sylvester's theorem (Amundson, 1966; Toor, 1964) enables us to evaluate $[f]$ in terms of the matrix $[D]$ and its eigenvalues $\hat{D}_i$ by use of the formula

$$f\{[D]\} = \sum_j \hat{f}_j(\hat{D}_j) \frac{\prod_{i \neq j} \{[D] - \hat{D}_i \ulcorner I \lrcorner\}}{\prod_{i \neq j} \{\hat{D}_j - \hat{D}_i\}} \tag{134}$$

The use of (134) for evaluating $[f]$ avoids the necessity of evaluating $[P]$. Explicitly for a ternary system we have

$$[f] = \hat{f}_1(\hat{D}_1) \frac{\begin{bmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{bmatrix} - \hat{D}_2 \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}}{\hat{D}_1 - \hat{D}_2} + $$

$$+ \hat{f}_2(\hat{D}_2) \frac{\begin{bmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{bmatrix} - \hat{D}_1 \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}}{\hat{D}_2 - \hat{D}_1} \tag{135}$$

Once $[f]$ is evaluated from (132) or (135), the composition profiles can be calculated from equation (131).

III.4.b Multicomponent 'Film' Model for Finite Mass Transfer Rates

Let us consider steady-state uni-dimensional diffusion in a non-reacting n-component fluid mixture at constant temperature. It is assumed that the compositions at the two ends of the diffusion path– a 'film' of thickness δ—are known and these remain fixed during the duration of the transfer process. It is required to determine the composition profiles and the constituent total molar fluxes N_i. We are in fact considering an alternative approach to the problem considered in sections III.1 and III.2. Here we consider the general case of a non-ideal fluid mixture.

Using the linearized theory approximation, i.e. c $[D]$ remains constant along the diffusion path, the equations of continuity (112) reduce to

$$u\,\frac{d(x)}{dz} = [D]\frac{d^2(x)}{dz^2} \tag{136}$$

where u is the molar average mixture velocity given by

$$u = N_t/c \tag{137}$$

From equations (70) and (71) we see that the constituent and total mixture fluxes are z-invariant. It will be assumed that the determinancy condition (72) is available and that the parameters ν_i are specified.

In proceeding with the solution of (136) we premultiply by $[P]^{-1}$ to obtain a series of $n-1$ equations

$$u\,\frac{d\hat{x}_i}{dz} = \hat{D}_i\,\frac{d^2\hat{x}_i}{dz^2}, \qquad i = 1,2,\ldots n-1 \tag{138}$$

which are subject to the transformed boundary conditions

$$\begin{aligned} &\text{at } z = 0, \quad \hat{x}_i = \hat{x}_{i0}, \\ &\text{at } z = \delta, \quad \hat{x}_i = \hat{x}_{i\delta}, \end{aligned} \qquad i = 1,2,\ldots n-1 \tag{139}$$

The solution to the corresponding binary diffusion problem is available (see BSL and also compare with equations (81)–(84)) and therefore the solution to the $n-1$ pseudo diffusion problems can be written down simply. Thus the pseudo composition profiles are given by

$$\hat{x}_i - \hat{x}_{i0} = \hat{f}_i(\hat{D}_i)\,\{\hat{x}_{i\delta} - \hat{x}_{i0}\}, \qquad i = 1,2,\ldots n-1 \tag{140}$$

where

$$\hat{f}_i(\hat{D}_i) = \frac{\exp\psi_i\eta - 1}{\exp\psi_i - 1}, \qquad i = 1,2,\ldots n-1 \tag{141}$$

in which the following parameters have been defined in addition to (77):

(i) pseudo-mass transfer rate factors

$$\psi_i \equiv N_t/\hat{k}^{\bullet}_i, \qquad i = 1,2,\ldots n-1 \tag{142}$$

(ii) pseudo-'zero flux' mass transfer coefficients

$$\hat{k}^{\bullet}_i \equiv c\,\hat{D}_i/\delta, \qquad i = 1,2,\ldots n-1 \tag{143}$$

where $\hat{D}_i$ represents the ith eigenvalue of $[D]$.

Equations (140), (141) give the composition profiles in terms of pseudo-variables; the original composition profiles can be recovered by applying the inverse $[P]$ transformation to obtain

$$(x - x_0) = [f]\,(x_\delta - x_0) \tag{144}$$

where the solution matrix $[f]$ can be obtained from (132) or (135).

The pseudo diffusion fluxes $\hat{J}_i$ vary from $z = 0$ to $z = \delta$; the fluxes at $z = 0$ being given by

$$\hat{J}_{i0} = -c\,\hat{D}_i \frac{d\hat{x}_i}{dz}\bigg|_{z=0} = -\hat{k}_i \frac{d\hat{x}_i}{d\eta}\bigg|_{\eta=0}, \quad i = 1,2,\ldots n-1 \tag{145}$$

The composition gradients may be evaluated from (140), (141) to give

$$\hat{J}_{i0} = \hat{k}_i \frac{\psi_i}{\exp\psi_i - 1}(\hat{x}_{i0} - \hat{x}_{i\delta}), \quad i = 1,2,\ldots n-1 \tag{146}$$

The factor $\psi_i/(\exp\psi_i - 1)$ shows the effect of finite mass transfer rates ($N_t \neq 0$) on the transfer coefficient $\hat{k}_i$. We may therefore define pseudo-'finite flux' mass transfer coefficients $\hat{k}_i^\bullet$ by

$$\hat{k}_i^\bullet = \frac{\hat{J}_{i0}}{\hat{x}_{i0} - \hat{x}_{i\delta}} = \hat{k}_i \frac{\psi_i}{\exp\psi_i - 1}, \quad i = 1,2,\ldots n-1 \tag{147}$$

In the limiting case of zero net mass transfer rate ($N_t \to 0$), we have $\psi_i \to 0$ and therefore

$$\lim_{N_t \to 0} \hat{k}_i^\bullet = \hat{k}_i, \quad i = 1,2,\ldots n-1 \tag{148}$$

The transfer coefficient $\hat{k}_i$ may therefore be interpreted as the limiting value of the mass transfer coefficient obtained under vanishingly small net rate of mass transfer. This zero flux coefficient $\hat{k}_i$ requires correction for finite transfer rates and the correction factor to be used in $\psi_i/(\exp\psi_i - 1)$. When there is a net transfer of material *out of* the phase under consideration (e.g. condensation of a vapour mixture), the ψ_i's are negative and the correction factors are greater than unity; there is an *increase* in the mass transfer coefficients due to finite transfer rates. On the other hand when material is transferred *into* the phase under consideration (e.g. evaporation into a gaseous stream), the rate factors ψ_i are positive, the correction factors are less than unity and the effect of the finite transfer rates is to *decrease* the mass transfer coefficients.

We may therefore multiply the matrix equation giving the pseudo-diffusion fluxes:

$$(\hat{J}_0) = \left\lceil \hat{k}^\bullet \right\rfloor (\hat{x}_0 - \hat{x}_\delta) \tag{149}$$

by $[P]$ to give the actual diffusion fluxes

$$(J_0) = [k^\bullet]\,(x_0 - x_\delta) \tag{150}$$

where the matrix of finite flux mass transfer coefficients is given by

$$[k^\bullet] = [P] \ulcorner \hat{k}^\bullet \lrcorner [P]^{-1} \tag{151}$$

and may also be obtained by use of Sylvester's theorem, equation (134). For a ternary system we have $[k^\bullet]$ given explicitly as

$$[k^\bullet] = \hat{k}_1^\bullet \left\{ \frac{[D] - \hat{D}_2 \ulcorner I \lrcorner}{\hat{D}_1 - \hat{D}_2} \right\} + \hat{k}_2^\bullet \left\{ \frac{[D] - \hat{D}_1 \ulcorner I \lrcorner}{\hat{D}_2 - \hat{D}_1} \right\} \tag{151a}$$

The total fluxes N_i are calculated from these diffusion fluxes J_{i0} by use of equations (103)–(105) with the y_{i0} being replaced by x_{i0}. Since the calculation of the matrix of finite flux coefficients $[k^\bullet]$ requires prior knowledge of the mixture total flux, it is clear that a trial and error procedure is involved. A stable iteration procedure is as follows:

STEP I. Calculate the elements of the matrix of diffusion coefficients $[D]$. Since the elements of $[D]$ are dependent on composition, this matrix must be estimated at some mean composition between x_{i0} and $x_{i\delta}$. The eigenvalues $\hat{D}_i$ of $[D]$ are obtained and the pseudo-'zero flux' mass transfer coefficients $\hat{k}_i$ calculated from equations (143).

STEP II. The correction factors $\psi_i/(\exp\psi_i - 1)$ are all assumed to be unity

STEP III. The pseudo-finite flux mass transfer coefficients $\hat{k}_i^\bullet$ are calculated from equations (147) and the matrix of finite flux coefficients $[k^\bullet]$ calculated from (151) or from Sylvester's theorem (e.g. (151a)).

STEP IV. The diffusion fluxes J_{i0} are then calculated from (150) and the total fluxes N_i determined from (103)–(105).

STEP V. With this estimate of N_i, the correction factors $\psi_i/(\exp\psi_i - 1)$ may be re-evaluated and the steps III–V repeated till convergence is obtained on the net mixture flux N_t.

For the case of equimolar counter diffusion ($N_t = 0$), the above procedure simplifies considerably because the correction factors do reduce to unity and therefore the finite flux coefficients equal the zero flux coefficients (cf. equation (148)).

It is important to appreciate the difference between the 'film' model for multicomponent mass transfer considered above and that developed in Sections III.1 and III.2. The linearized theory film model assumes $c\ [D]$ is constant and is therefore an approximation *even for ideal gas mixtures.* The procedure developed by Krishna and Standart (1976b), discussed in III.1, is *exact* for ideal gas mixtures. For liquid mixtures, the procedure of Krishna (1976a), discussed in III.2, represents an approximation in which the Maxwell-Stefan diffusion coefficients are assumed to be constant over the diffusion path. This approximate procedure is to be preferred when complete thermodynamic information on the activity coefficients γ_i is available together with information on the $\mathcal{D}_{ik}$. When only experimental information on the matrix $[D]$ is available for liquid mixtures, then the linearized theory approach is to be preferred because it does not require additional thermodynamic information.

An important difference between the linearized theory approach, and the Krishna and Standart matrix solution is that in the former approach, only the net mixture flux N_t

appears in the flux corrections whereas in the latter method each individual flux offers its own intrinsic correction (cf. equation (100)).

III.4.c Multicomponent Penetration Model for Finite Mass Transfer Rates

Consider multicomponent diffusion in a one-dimensional semi-infinite fluid system. The system is initially of uniform composition (x_∞) and at time $t = 0$, the interfacial composition is instantaneously changed to a value (x_0) and maintained at this value for all time $t > 0$. With the assumption that $c\,[D]$ remains constant during the diffusion process, the variations of the fluid compositions are described by the matrix differential equation (cf. equation (112))

$$\frac{\partial(x)}{\partial t} + u\,\frac{\partial(x)}{\partial z} = [D]\frac{\partial^2(x)}{\partial z^2} \tag{152}$$

with the boundary conditions

$$\begin{aligned} &t \leqq 0, \quad z > 0, \quad (x) = (x_\infty) \\ &t > 0, \quad z = 0, \quad (x) = (x_0) \\ &t > 0, \quad z = \infty, \quad (x) = (x_\infty) \end{aligned} \tag{153}$$

The solution to the corresponding binary diffusion problem is available (BSL) and therefore once the equation (152) is uncoupled by premultiplication with $[P]^{-1}$, the solution to the set of pseudo-binary problems can be written down. The uncoupling procedure is exactly as described in the previous examples.

The diffusion flux at any instant of time is therefore given by

$$\hat{J}_{i0} = \hat{k}^{\bullet}_{i}\{\hat{x}_{i0} - \hat{x}_{i\infty}\}, \qquad i = 1,2,\ldots n-1 \tag{154}$$

where the pseudo-‘finite flux’ (instantaneous) mass transfer coefficients are given by (BSL; Stewart and Prober, 1964)

$$\hat{k}^{\bullet}_{i} = \hat{k}_{i}\left[1 + \operatorname{erf}\left\{\frac{\Psi_i}{\sqrt{\pi}}\right\}\right]^{-1} \exp\left\{-\frac{\Psi_i^2}{\pi}\right\} \qquad i = 1,2,\ldots n-1 \tag{155}$$

with erf the error function and with the pseudo-‘zero flux’ mass transfer coefficients obtained from

$$\hat{k}_{i} = c\left[\frac{\hat{D}_i}{\pi t}\right]^{1/2}, \qquad i = 1,2,\ldots n-1 \tag{156}$$

The dimensionless rate factors Ψ_i in (155) are given by

$$\Psi_i = N_{t0}/\hat{k}_i, \qquad i = 1,2,\ldots n-1 \tag{157}$$

Equation (151) or (151a) may be used to calculate the matrix of finite flux mass transfer coefficients, $[k^\bullet]$.

Equation (156) gives the instantaneous value of the pseudo-zero flux mass transfer coefficients; the averaged value over the interval of time 0 to t is obtained as $2\ c\ (\hat{D}_i/\pi t)^{1/2}$. For a comparison of the film and penetration theory predictions for multicomponent mass transfer see Krishna (1978a, 1978b).

IV. TURBULENT DIFFUSION

For turbulent flow condtions the differential equations of continuity apply in their time averaged form. Thus we have (BSL)

$$c\ \frac{dx_i}{dt} = c\ \frac{\partial x_i}{\partial t} + c\,\mathbf{u}\cdot\nabla x_i = -\nabla\cdot J_i - \nabla\cdot J_i^t, \qquad i=1,2,\ldots n-1 \tag{158}$$

where the composition x_i and the velocity $\mathbf{u}$ are considered to represent time averaged values. $\mathbf{J}_i$ is the diffusion flux due to molecular processes and $\mathbf{J}_i^t$ represents the turbulent diffusion flux. We may extend the discussion on molecular diffusional transport to the turbulent case by writing the following constitutive relation for the turbulent diffusion flux (cf. equation (22))

$$(\mathbf{J}^t) = -\ c\ [D^t]\ (\ \nabla\ x) \tag{159}$$

where $[D^t]$ is the matrix of turbulent eddy diffusivities (Toor, 1960; Stewart, 1973).

If transfer takes place entirely by turbulent mixing, as assumed for example in mixing length theories, then the D^t_{ij} are independent of molecular diffusivities (Toor, 1960). This condition is approximately realized in binary systems where experiment and theory indicate that the effect of the molecular Schmidt number on the turbulent diffusivity is not large. It seems reasonable at least as a first approximation to assume that the same condition holds in a multicomponent system. If it is further assumed that the magnitude of the mixture flux N_t has no effect on the turbulent diffusivities (which is equivalent to assuming that the velocity $\mathbf{u} = N_t/c$ is negligible compared to the turbulent core velocity so that its effect on the turbulence level can be neglected) then the D^t_{ij} are fixed by the system hydrodynamics and are independent of the number of species present. With these assumptions there can be no turbulent diffusional interactions between species and the matrix $[D^t]$ must degenerate to a scalar times the identity matrix,

$$[D^t] = D^t\ \ulcorner I \lrcorner \tag{160}$$

On combining equations (158)–(160) and using equation (22) we obtain

$$\frac{\partial(x)}{\partial t} + \mathbf{u}\ \cdot\ \nabla\ (x) = \nabla\ \cdot\ \{([D] + D^t\ \ulcorner I \lrcorner\ )\ \nabla\ (x)\} \tag{161}$$

which equation can be diagonalized by assuming $c\ [D]$ is constant along the diffusion path (Standart and Krishna, 1979; Stewart, 1973). Note that D^t can, and does, vary along the diffusion path and vanishes at the interface.

As the level of turbulence increases, the coupling becomes weaker and for completely turbulent conditions the right hand side of (161) reduces to a diagonal form. So in general we may expect multicomponent diffusional coupling to be less significant in turbulent flow. von Behren *et al* (1972) undertook an experimental study of ternary mass transfer in turbulent flow; their theoretical analysis is plagued by a conceptual error as pointed out by Stewart (1973).

V. ISOTHERMAL MASS TRANSFER AT A PHASE BOUNDARY

So far we have considered molecular and turbulent n-component diffusion within a single fluid phase and discussed methods for calculation of composition profiles and fluxes. In most separation processes, and in may other practical situations where mass transfer is important, transport of material from one phase to another is involved. In most practical situations, the flow is turbulent and the flow field is inadequately specified; both molecular and turbulent eddy diffusion are involved. A complete theoretical analysis is not possible and one has to rely on empirical and semi-empirical methods for predicting the transfer rates. Excellent discussions on interphase mass transfer in binary systems are available in the literature (e.g. BSL; Sherwood, Pigford and Wilke, 1975); here we consider the formalisms associated with multicomponent mass transfer across phase boundaries.

V.1. Total Fluxes, Diffusion Fluxes

Consider a two fluid–fluid phase system; let 'y' denote the lighter phase and 'x' the heavier phase. It is easy to show by a material balance that if N_i is the normal constituent material in a given phase at the interface and with respect to it,

$$N_i^y = N_i^x = N_i, \qquad i = 1,2,\ldots n-1 \tag{162}$$

The only assumptions required are that no surface reaction is occurring and there are no constituent adsorptions at the interface. The common flux may be called a *phase invariant* (Standart, 1964).

If we further assume that (i) the average state of each phase can be characterised by bulk properties (denoted by subscript b), (ii) that the transport rates in the interfacial region in directions tangent to the interface are negligible compared to the normal interphase transport rates and (iii) under unsteady state conditions, the rate of accumulation in the interfacial region is negligible compared to the normal interphase transport rate (or at least that the average rate of accumulation is negligible), we can show that

$$N_{ib}^y = N_i = N_{ib}^x, \qquad i = 1,2,\ldots n \tag{163}$$

While assumption (i) is generally justifiable, assumption (ii) applies best when the interfacial region is a thin zone near the phase boundary with the bulk phases well mixed as is implied in many theories of mass transfer (e.g. film, penetration and boundary layer theories). Assumption (iii) is satisfied for many quasistationary processes and if the thin zone assumption is satisfied, it will be a good approximation even in many unstationary cases.

The mixture molar transport flux, N_t, given by

$$N_t = \sum_{i=1}^{n} N_i \tag{164}$$

is also a phase invariant.

Just as in the treatment of intraphase diffusion, it is convenient to define diffusion fluxes with respect to the total mixture flux N_t. If we consider the 'x' phase explicitly we may write the diffusion flux in that phase as

$$J_i^x = N_i^x - x_i N_t^x = N_i - x_i N_t, \quad i = 1,2,\ldots n \tag{165}$$

We see that while the total fluxes N_i are phase invariants the diffusion fluxes J_i are not; indeed due to the variation of the compositions x_i from the bulk phase to the interface, they vary within the phase from the bulk to the interface. In processing operations the bulk phase compositions are measurable and of interest and therefore it is usually the bulk diffusion fluxes,

$$J_{ib}^x = N_i - x_{ib} N_t, \qquad i = 1,2,\ldots n \tag{166}$$

which are useful from a computational point of view. We may write relations parallel to (165) and (166) for the 'y' phase.

V.2 Interphase Mass Transport Rate Relations, Multicomponent Mass Transfer Coefficients

In the discussions on intraphase diffusion, the constitutive relations for the diffusion fluxes J_i were obtained by postulating linear relations between the diffusion fluxes and the composition *gradients* (cf. equation (21)). These constitutive relations describe the diffusion characteristics *locally*. The theory of TIP was used to show that chemical potential gradients are more 'fundamental' measures of the driving forces for diffusion. In extending the treatment of intraphase diffusion to interphase mass transfer across phase boundaries, we must consider differences in the chemical potentials

$$\nabla \mu_i^x = \mu_{iI}^x - \mu_{ib}^x, \qquad i = 1,2,\ldots n \tag{167}$$

between the interface (subscript I) and the bulk fluid phase to represent the proper driving forces for interphase mass transport. As in intraphase diffusion, it is convenient for many practical problems to adopt more 'practical' driving forces such as partial pressure differences (Δp), concentration differences (Δc), humidity differences (ΔY)

etc. Here we adopt composition (mole fraction) differences as practical driving forces; these driving forces are simple to use in many practical separation processes such as distillation, absorption, condensation, extraction etc. Thus we use for phase 'x' the driving forces

$$\Delta x_i = x_{iI} - x_{ib}, \qquad i = 1,2,\ldots n \tag{168}$$

where we consider transfer from the y to the x phase as positive.

Now, for interphase mass transfer in two-component systems it is usual to define the binary mass transfer coefficient, $k^\bullet_{xb12}$, by

$$J^x_{1b} = k^\bullet_{xb12}\Delta x_1 \tag{169}$$

where the superscript black dot ● on the mass transfer coefficient reminds us that interphase transfer coefficients defined in terms of composition differences depend in general on the rates of transfer N_i. The subscript b on the mass transfer coefficient emphasises the fact that the transfer coefficient has been defined in terms of the bulk diffusion flux J^x_{1b}. If the interfacial diffusion fluxes are considered then we have correspondingly

$$J^x_{1I} \equiv N_1 - x_{1I}(N_1 + N_2) = k^\bullet_{xI12}\Delta x_1 \tag{170}$$

The finite flux mass transfer coefficients $k^\bullet_{xb12}$ and $k^\bullet_{xI12}$ are not equal in general except for vanishing rates of transfer. The determination of these finite flux coefficeints from the zero flux coefficients requires the use of various simplified hydrodynamic models for mass transfer (film, penetration theories) and is discussed at length in BSL.

For the general n-component case, there are $n-1$ independent composition difference driving forces since

$$\sum_{i=1}^{n} \Delta x_i = 0 \tag{171}$$

and also $n-1$ independent diffusion fluxes as for the analogous y phase relations. As an extension of the binary rate relation (169) we must consider writing the constitutive relations

$$J^x_{ib} = \sum_{k=1}^{n-1} k^\bullet_{xbik}\Delta x_k, \qquad i = 1,2,\ldots n-1 \tag{172}$$

or in matrix notation

$$(J^x_b) = [k^\bullet_{xb}]\,(\Delta x) \tag{173}$$

The mass transfer characteristics of a particular phase are described by a matrix of mass transfer coefficients of dimension $n-1 \times n-1$. It is important to appreciate that the actual magnitudes of the elements $k^\bullet_{xbij}$ depend on (i) the (arbitrary) numbering of the constituents in the mixture, (ii) the magnitudes and directions of the fluxes N_i at the position under consideration and therefore on the magnitudes and signs of the driving forces Δx_i and (iii) on the (basically arbitrary) choice of using bulk or interfacial diffusion fluxes.

In the limit of vanishing transfer rates ($N_i \to 0$) the matrix of finite flux mass transfer coefficients equals the matrix of zero flux mass transfer coefficients. Thus

$$\lim_{\substack{N_i \to 0,\\ i=1,2,\ldots n}} [k^{\bullet}_{xb}] = [k_{xb}] \tag{174}$$

which serves to define the zero flux coefficients k_{xbij}, which are the same for the bulk and interface.

V.3 Estimation of Multicomponent Mass Transfer Coefficients

Most experimental research works in the past tended to concentrate on two-component systems and empirical correlations for the binary mass transfer coefficient are available for various system geometries and hydrodynamics (see for example Sherwood, Pigford and Wilke, 1975). Such correlations are typically of the form

$$\frac{k_{xij}\, d}{c\, \mathscr{D}_{xij}} = a\,(\mathrm{Re})^b \left[\frac{\mu_x}{\rho\, \mathscr{D}_{xij}}\right]^c \tag{175}$$

where d is some characteristic dimension in the mass transfer equipment; k_{xij} is the zero flux binary mass transfer coefficient for the pair i-j; $\mathscr{D}_{xij}$ is the zero flux diffusion coefficient in the 'x' phase for the pair i-j; a, b and c are experimentally determined 'constants'. The coefficient k_{xij} calculated from such correlations needs to be corrected for finite transfer rates before use in design equations. The film theory correction for finite transfer rates is given in equation (82) while the penetration model correction is given in (155).

Since binary mass transfer experimental data are available in the literature it is desirable to be able to predict the matrix $[k^{\bullet}_{xb}]$ from binary transport data alone. Such predictions are possible for multicomponent gas phase transport; for multicomponent liquid phase transport, it is essential to have measured liquid phase multicomponent diffusion data ($[D_x]$).

With the linearized theory of multicomponent mass transfer, the procedure for calculating the matrix $[k^{\bullet}_{xb}]$ is as follows (Toor, 1964; Stewart and Prober, 1964):

STEP I. For conditions prevailing at any position in the mass transfer equipment, it is assumed that the compositions in the bulk fluid phase, x_{ib}, and at the interface, x_{iI}, are known. The matrix of diffusion coefficients $[D]$ is estimated at some mean composition between x_{ib} and x_{iI}. For ideal gas mixtures the matrix $[D]$ can be estimated from the diffusion coefficients of the binary pairs $\mathscr{D}_{yik}$. For liquid mixtures it may be necessary to determine $[D]$ by experimental measurement.

STEP II. The eigenvalues of $\hat{D}_i$ of $[D]$ are calculated. As has been seen in sections III.3 and III.4, once the governing differential equations are uncoupled by pre-multiplication with $[P]^{-1}$, each pseudo-species behaves as though it were in a binary mixture with a characteristic diffusion coefficient $\hat{D}_i$. Substitution of $\hat{D}_i$ in place of $\mathcal{D}_{xij}$ in mass transfer correlations of the type in equation (175) would therefore yield the pseudo-'zero flux' mass transfer coefficients, $\hat{k}_i$.

STEP III. The pseudo 'zero flux' mass transfer coefficients need to be corrected for finite mass transfer rates. Corrections may proceed by use of the film or penetration theories as discussed in III.4 b and III.4.c. The pseudo 'finite flux' mass transfer coefficients $\hat{k}_i^\bullet$ are thus obtained.

STEP IV. The matrix $[k_{xb}^\bullet]$ is then obtained by use of (151) or (151a).

An alternative procedure for estimating $[k_b^\bullet]$ from binary transport data alone is using the Krishna and Standart matrix method for solution to the Maxwell-Stefan equations, discussed in III.1. Their procedure is particularly applicable to gas phase transport and does not make the assumption of a constant matrix of diffusion coefficients. The outline of the procedure is as follows:

STEP I. From the knowledge of the binary diffusion coefficients $\mathcal{D}_{yik}$ of the constituent binary pairs in the multicomponent mixture, calculate the corresponding mass transfer coefficients k_{yik} from the correlation of type (175).

STEP II. Calculate the elements of the matrix $[B_0]$ from equations (91) and (92), using the bulk phase compositions y_{ib}.

STEP III. The matrix of 'zero flux' mass transfer coefficients $[k_{yb}]$ is obtained from inversion of $[B_0]$ (cf. equation (101)).

STEP IV. The matrix of 'zero flux' mass transfer coefficients is corrected for finite rates of transfer by post multiplication with the matrix of correction factors, $[\Xi]$, calculated as outlined in III.1.

Calculations of $[k_{xb}^\bullet]$ must be carried out for local conditions prevailing in the apparatus; it is generally not permissible to assume that these mass transfer coefficients are constant over the entire contracting equipment.

Now, once the matrix $[k_{xb}^\bullet]$ has been estimated we are in a position to calculate the $n-1$ diffusion fluxes in the phase 'x', J_{ib}^x, from equation (173). There still remains the problem of determining the n total fluxes N_i from a knowledge of these diffusion fluxes; this problem has been termed the 'bootstrap' problem (Krishna and Standart, 1976c).

V.4. The Bootstrap Problem and Solution

As discussed in III.1 the solution to the bootstrap problem requires an additional determinancy condition. It is usually possible to write this condition in the form given by equation (72). The bootstrap solution is therefore given by equations (103)–(105), where in general the bulk fluid phase compositions x_{ib} replace the y_{i0}. It is useful and convenient to represent equations (103) in the compact $n-1$ dimensional matrix notation as

$$(N) = [\beta^x]\,(J_b^x) \qquad (176)$$

where the elements of the 'bootstrap solution matrix', $[\beta^x]$, are given by

$$\beta_{ik}^x = \delta_{ik} - x_{ib}\,\Lambda_k, \qquad i,k = 1,2,\ldots n-1 \qquad (177)$$

with the element Λ_k given by relations analogous to (105). The nth flux N_n is obtained from equation (104).

Combination of equations (173) and (176) gives

$$(N) = [\beta^x]\,[k^{\bullet}_{xb}]\,(\Delta x) \tag{178}$$

We may re-write equation (178) in terms of a matrix of 'total' mass transfer coefficients, $[W_x]$, as

$$(N) = [W_x]\,(\Delta x) \tag{179}$$

so that

$$[W_x] = [\beta^x]\,[k^{\bullet}_{xb}] \tag{180}$$

The bootstrap solution for the 'y' phase may be written down in a manner analogous to the above relations.

V.5. 'Total' vs. 'Diffusive' Mass Transfer Coefficients

The intrinsic mass transfer characteristics of a particular phase are correctly portrayed by the transfer coefficients $[k^{\bullet}_{xb}]$ defined in terms of the *diffusive* fluxes J^x_{ib}. The 'total' transfer coefficients $[W_x]$ defined in (179) include not only the proper diffusive mass transfer processes but also convective transports which depend on the overall system conditions and constraints as well as the driving forces. As we have stated it is the 'diffusive' coefficients $[k^{\bullet}_{xb}]$ which are capable of being predicted from binary transport data. It is only when conditions of equimolar counter-transfer prevail (zero convective transport, $N_t = 0$) that the 'total' transport coefficients $[W_x]$ are useful because for this case they are identical with the 'diffusive' transport coefficients (for this case $[\beta^x]$ reduces to the identity matrix).

VI. INTERACTION PHENOMENA IN MULTICOMPONENT MASS TRANSFER

The possibility of coupling between species transfers in systems of three or more components distinguish multicomponent systems from simpler two-component systems. This coupling arises due to the presence of cross coefficients in the matrices of diffusion coefficients and mass transfer coefficients. Thus if we consider a ternary gas mixture we see that the elements D_{y12} and D_{y21} of the matrix $[D_y]$ are given by equations (64) and (65). When the diffusion coefficients of the binary pairs making up the ternary mixture are not all equal, i.e. $\mathscr{D}_{y12} \neq \mathscr{D}_{y13} \neq \mathscr{D}_{y23}$, then the cross coefficients D_{y12} and D_{y21} will be non-zero. The larger the differences between the transfer facilities of the constituent binary pairs, the larger will be the magnitudes of these cross coefficients. The signs of D_{y12} and D_{y21} will depend on the numbering of the species. Thus if we choose the system numbering such that the diffusion coefficient of the binary pair

1-2, $\mathcal{D}_{y12}$, is the smallest, then both D_{y12} and D_{y21} will be positive. Coupling effects in ternary gas transport will be large when D_{y12} is a significant proportion of D_{y11} and D_{y21} is a significant proportion of D_{y22}. For liquid mixtures the thermodynamic non-ideality of the mixture also contributes to non-zero cross coefficients. If we again consider a ternary mixture, equation (61) shows that the cross coefficient D_{x12} will be given by

$$D_{x12} = \frac{\Gamma_{12}\bar{D}_{13}(x_1\bar{D}_{23} + (1 - x_1)\,\bar{D}_{12}) + \Gamma_{22}x_1\,\bar{D}_{23}\,(\bar{D}_{13} - \bar{D}_{12})}{x_1\bar{D}_{23} + x_2\bar{D}_{13} + x_3\bar{D}_{12}} \tag{181}$$

We see therefore that the thermodynamic factors Γ_{ij}, given by equation (40), also contribute to D_{xij} $(i{\neq}j)$. The large cross coefficients possible in non-ideal liquid mixtures is exemplified by the system polystyrene (1)–cyclohexane (2)–toluene (3) for which Cussler and Lightfoot (1965) measured $|D_{x12}/D_{x11}| > 1$ in certain concentration regions.

Coupling effects are weaker in systems with combined molecular and turbulent eddy transport, as explained in section IV. For mass transfer across phase boundaries where combined modes of transport prevail, we may therefore expect slightly diminished coupling from purely molecular transport mechanism. The extent by which coupling effects are diminished are reflected in the mass transfer correlations of the form (175) where we see that $k_{xij} \propto \mathcal{D}_{xij}{}^{1-c}$.

Consider the matrix of zero flux coefficients $[k_{xb}]$ for a three-component mixture. We might expect the cross-coefficient k_{xb12}, for example, to be proportional to the difference between the transfer coefficients of the binary pairs 1-3 and 1-2, i.e.

$$k_{xb12} \propto \bar{k}_{x13} - \bar{k}_{x12} \tag{182}$$

and similarly for k_{xb21} we have

$$k_{xb21} \propto \bar{k}_{x23} - \bar{k}_{x12} \tag{183}$$

It is therefore possible to choose the system numbering such that the elements of $[k_{xb}]$ are all positive (the main coefficients k_{xii} will be positive in most practical cases, whatever the system numbering).

The presence of non-zero cross-coefficients $k^{\bullet}_{xbij}$ $(i{\neq}j)$ imparts to the multicomponent system transfer characteristics which set it apart from binary systems; we shall illustrate these characteristics by considering the simplest case of a multicomponent system—a ternary mixture. The rate relations (172) may be written explicitly as

$$J^x_{1b} = k^{\bullet}_{xb11}\,\Delta x_1 + k^{\bullet}_{xb12}\,\Delta x_2 \tag{184}$$

$$J^x_{2b} = k^{\bullet}_{xb21}\,\Delta x_1 + k^{\bullet}_{xb22}\,\Delta x_2 \tag{185}$$

In proceeding with the discussions it is convenient to define the following ratios of the elements of $[k^{\bullet}_{xb}]$:

$$\Upsilon = \frac{k^\bullet_{xb11}}{k^\bullet_{xb22}};\ \Omega_{12} = \frac{k^\bullet_{xb12}}{k^\bullet_{xb11}};\ \Omega_{21} = \frac{k^\bullet_{xb21}}{k^\bullet_{xb22}} \tag{186}$$

Further, we define the ratio of driving forces for components 1 and 2,

$$\alpha = \frac{\Delta x_1}{\Delta x_2} \tag{187}$$

With these definitions the rate relations (184) and (185) may be written as

$$\mathcal{J}^x_{1b} = \Upsilon\, k^\bullet_{xb22}\,(1 + \Omega_{12}/\alpha)\,\Delta x_1 \tag{188}$$

$$\mathcal{J}^x_{2b} = k^\bullet_{xb22}\,(1 + \Omega_{21}\,\alpha)\,\Delta x_2 \tag{189}$$

Consider equation (188). If the system operating conditions are such that

$$\alpha = -\,\Omega_{12} \tag{190}$$

then we see from (188) that we must necessarily have

$$\mathcal{J}^x_{1b} = 0 \qquad |\Delta x_1 \neq 0| \tag{191}$$

without the vanishing of the driving force Δx_1; a *mass transfer barrier* may be said to exist for component 1.

For the range of values of α given by

$$-\,\Omega_{12} < \alpha < 0 \tag{192}$$

we must have (cf. equation (188))

$$\mathcal{J}^x_1\,\Delta x_1 < 0 \tag{193}$$

i.e. the species 1 transfers in a direction opposite to that dictated by its intrinsic driving force Δx_1; this phenomenon may be termed *reverse mass transfer.*

Another interesting behaviour is observed for component 1 when its driving force vanishes, i.e. $\Delta x_1 = 0$; for this case

$$\mathcal{J}^x_{1b} = k^\bullet_{xb12}\,\Delta x_2 \neq 0 \qquad |\Delta x_1 = 0| \tag{194}$$

This phenomenon of transfer of a component in the absence of its intrinsic driving force may be termed *osmotic mass transfer.*

The three phenomena described above may be called *interaction* phenomena. Toor (1957) discussed the three phenomena in detail in the context of ternary gas diffusion; here we have presented a generalized analysis. Since binary mass transfer coefficients $k^\bullet_{xb12}$ are always expected to be positive and non-zero, it is easy to see from equation (169) that such interaction phenomena cannot be observed for a binary system.

At first sight it might appear that the second law of thermodynamics is violated for reverse mass transfer to occur. This is not so. One process may depart from equilibrium in such a sense as to consume entropy provided it is coupled to another process which produces entropy even faster. This is of course the basic principle of any pump, whether it moves water uphill or moves heat towards a higher temperature region (Wei, 1966). For the second law requirement, $\sigma > 0$, to hold it is allowable for σ_1 to be < 0, corresponding to reverse diffusion for 1, provided σ_2 and σ_3, due to species 2 and 3 diffusion, be such that the overall entropy production rate is positive ($\sigma_1 + \sigma_2 + \sigma_3 > 0$).

Duncan and Toor (1962) experimentally detected the three interaction phenomena for diffusion in the gaseous system: nitrogen (1)–hydrogen (2)–carbon dioxide (3) in a two-bulb diffusion cell. Their experimental results also confirm the applicability of the Maxwell-Stefan diffusion equations; this conclusion was also reached by Carty and Schrodt (1975), Bres and Hatzfeld (1977) and Hesse and Hugo (1972).

The ratio of driving forces α plays an important role in enhancing diffusional interaction effects in multicomponent mass transfer. Thus a small cross-coefficient $k^{\bullet}_{xb12}$ may be linked to a large Δx_2 to result in large interaction effects.

VII. APPROXIMATE TREATMENTS OF MULTICOMPONENT MASS TRANSFER

The basic difficulty with the full treatment of multicomponent mass transfer arises due to the coupling between the species transfers, i.e. dependence of the flux of species i on the driving forces of species j ($j \neq i$); this is in contrast to a simple two-component system in which the flux of a species is dependent only on its own driving force. This coupling effect, quantified by the presence of cross diffusion and mass transfer coefficients, complicates the solution of the differential equations governing the diffusion process and we have to resort to uncoupling procedures or attempt a brute-force numerical solution. The simplicity of the binary mass transfer formulations (equations (13), (169)) coupled with the relative abundance of binary experimental work and correlations and the extreme paucity of even ternary mass transfer data have prompted many authors in the past to try to *model* multicomponent mass transfer as pseudo-binaries. This 'force-fit' has been attempted in two ways: (i) by use of a 'modified' driving force or by (ii) by defining various 'effective' diffusion coefficients. We consider these in turn.

Toor (1957) attempted to model ternary gas diffusion by a approximate method which involved the definition of a 'generalized' driving force. His approximate relationship, representing an approximate solution to the Maxwell-Stefan diffusion equations, displays the correct characteristics of ternary diffusion, i.e. it is successful in accounting for the three interaction phenomena discussed in section VI. The Toor (1957) approximate method is limited in its applicability to ternary systems and the procedure for generalization to the multicomponent case is not obvious. Toor's paper in 1957 represented the first concerted attack on the problem of multicomponent diffusion and served to kindle interest in this area and lead to the development of the linearized theory of multicomponent mass transfer in 1964. We will not consider this approximate method any further as neither its author nor others have used it recently because of the availability of more general and less complicated procedures. Other approaches based on modified driving forces (Konstantinov and Nikolaev, 1964; Shporin and Nikolaev, 1968; Shporin, Konstantinov and Nikolaev, 1968; Telyakov and Nikolaev, 1968) are based on an incorrect generalization of binary mass transfer driving forces and so do not warrant further discussion.

All effective diffusion coefficient approaches for gaseous mixtures start with the Maxwell-Stefan diffusion equations (59), modified to fit flux equations of the general form

$$\mathbf{N}_i = -c\ \mathcal{D}_{i,\text{eff}}\ \nabla y_i + \alpha_i y_i N_t, \tag{195}$$

There are three basic choices for α_i, giving three basic definitions for the effective diffusion coefficient $\mathcal{D}_{i,\text{eff}}$:

(1) Here we take $\alpha_i = 1$ and force fit the Maxwell-Stefan equations (59) into the form of (195) to obtain the effective diffusivity as (Hsu and Bird, 1960; Shain, 1961; Wilke, 1950)

$$\mathcal{D}_{i,\text{eff}} = \frac{\mathbf{N}_i - y_i \sum\limits_{j=1}^{n} \mathbf{N}_j}{\mathbf{N}_i \sum\limits_{\substack{j=1 \\ j\neq i}}^{n} \dfrac{y_j}{\mathcal{D}_{ij}} - y_i \sum\limits_{\substack{j=1 \\ j\neq i}}^{n} \dfrac{\mathbf{N}_j}{\mathcal{D}_{ij}}} \tag{196}$$

When all the diffusion coefficients $\mathcal{D}_{ij}$ are approximately equal to one another ($=\mathcal{D}$), equation (196) simplifies to give

$$\mathcal{D}_{i,\text{eff}} = \mathcal{D} \tag{197}$$

for all species (cf. equation (20) and discussion following it).

When component 1 diffuses through a mixture of stagnant gases ($\mathbf{N}_1 \neq 0$, $\mathbf{N}_2 = 0, \mathbf{N}_3 = 0, \ldots \mathbf{N}_n = 0$), the effective diffusion coefficient is obtained from equation (196) as

$$\mathcal{D}_{1,\text{eff}} = \frac{1 - y_1}{\sum\limits_{j=2}^{n} \dfrac{y_j}{\mathcal{D}_{1j}}} \tag{198}$$

Another case when (196) simplifies considerably is when we encounter diffusion of trace amounts of $1,2,\ldots n-1$ in a large excess of species n ($y_1 \simeq 0$, $y_2 \simeq 0$, $y_3 \simeq 0 \ldots y_{n-1} \simeq 0, y_n \simeq 1$); for this case

$$\mathcal{D}_{i,\text{eff}} = \mathcal{D}_{in}, \qquad i = 1,2,\ldots n-1 \tag{199}$$

For the three limiting cases above, the effective diffusion coefficient, given by equations (197), (198) and (199), is a system property; it may be used in place of the binary diffusivity in mass transfer correlations to give the effective coefficient for transfer of that particular species in the multicomponent mixture. The basic definition (196) shows that for the general case the effective diffusion coefficient must be a function of the rates of transfer $\mathbf{N}_i$ and average compositions not always known in advance of solving the problem.

(ii) The second basic definition of the effective diffusivity is obtained by taking $\alpha_i = 0$ and force fitting the Maxwell-Stefan equations (59) into the form (195) to obtain (Kubota, Yamanaka and Dalla Lana, 1969) the following expression for the effective diffusion coefficient:

$$\frac{1}{\mathcal{D}_{i,\text{eff}}} = \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{y_j}{\mathcal{D}_{ij}} \left[1 - \frac{y_i}{y_j} \frac{\mathbf{N}_j}{\mathbf{N}_i} \right] \tag{200}$$

The definition (200) is convenient when the flux ratios are known in advance, as is the case when we have diffusion controlled chemical reactions taking place on catalyst surfaces; the flux ratios in this case are fixed by the stoichiometry of the reaction.

(iii) The third possibility is to assume that the effective diffusion coefficient defined by (198) is valid in general for all diffusing species (Wilke, 1950):

$$\mathcal{D}_{i,\text{eff}} = \frac{1 - y_i}{\sum\limits_{\substack{j=1 \\ j \neq i}}^{n} \frac{y_j}{\mathcal{D}_{ij}}} \tag{201}$$

Clearly the above definition is exact for the diffusion of a single species through a mixture of stagnant gases. For other cases the relation (201) can only be considered approximate, having as its only virtue the fact that the calculation is based on system properties.

The primary advantage of the effective diffusivity definitions is their simplicity as their use permits the adaptation of binary mass transfer correlations, say of type (175), by replacing the binary diffusivity with the $\mathcal{D}_{i,\text{eff}}$.

The primary disadvantage of the use of $\mathcal{D}_{i,\text{eff}}$ is that these parameters are not, in general, system properties except for the limiting cases noted above. Further, they depend on the magnitude of the fluxes not always known in advance.

Generally in multicomponent systems, effective diffusivities do not have the physical significance of a diffusion coefficient since they may assume values ranging from minus to plus infinity (Toor and Sebulsky, 1961). The effective average diffusivity over a diffusion path is zero at a diffusion barrier, negative in the region of reverse diffusion and has a singularity at the osmotic diffusion point. Care must therefore be taken in drawing analogies between this quantity and a binary diffusion coefficient. Only when the effective diffusivity is positive, bounded and not a strong function of composition or fluxes is it possible to draw useful analogies.

For liquid mixtures, effective diffusion coefficients may be defined using the generalized Maxwell-Stefan equations (Lightfoot and Scattergood, 1965); comments similar to above would apply here as well.

We have so far seen the difficulties associated with the definitions of the effective diffusion coefficient for species i in the mixture. Using experimental data on multicomponent mass transfer, we may of course *calculate* pseudo-binary mass transfer coefficients, $\grave{k}_{xi}$, for each of the independent transferring species using the definition

$$J^{x}_{ib} = \grave{k}_{xi}\,\Delta x_i, \qquad i = 1,2,\ldots n-1 \tag{202}$$

We shall now show that these pseudo-binary coefficients $\grave{k}_{xi}$ are unsuitable as correlation or design parameters; we take the case of a ternary mixture for this purpose.

Comparison of equation (202) with (188) and (189) shows that

$$\grave{k}_{x1} = \Upsilon\, k^{\bullet}_{xb22}\,(1 + \Omega_{12}/\alpha) \tag{203}$$

$$\grave{k}_{x2} = k^{\bullet}_{xb22}\,(1 + \Omega_{21}\alpha) \tag{204}$$

The pseudo-binary mass transfer coefficient for the third component is dependent and is given, in view of equations (8), (171) and (202), as

$$\grave{k}_{x3} = \frac{\alpha\grave{k}_{x1} + \grave{k}_{x2}}{\alpha + 1} \tag{205}$$

It is clear from equations (203) and (204) that the coefficients $\grave{k}_{xi}$ depend directly on the ratio of driving forces α; this ratio changes with the operating conditions and the phase equilibrium behaviour of the multicomponent system. It is possible in a given separation column for the ratio α to suffer large changes in both magnitude and sign; the pseudo-binary coefficients $\grave{k}_{xi}$ would therefore also suffer large changes in magnitude, and possibly in sign, under conditions in which the hydrodynamics of the particular phase 'x' remained relatively constant. It would therefore be difficult, nay impossible, to obtain generally applicable correlations for the $\grave{k}_{xi}$ in terms of system hydrodynamics, physical and transport properties. These comments are reinforced below.

Under conditions of mass transfer barrier for 1 (cf. equation (191)) we have

$$\grave{k}_{x1} = 0 \tag{206}$$

and for operating conditions satisfying (192) we must have

$$\grave{k}_{x1} < 0 \tag{207}$$

while at the osmotic mass transfer point (equation (194))

$$\grave{k}_{x1} \rightarrow \pm\,\infty \tag{208}$$

Equations (206)–(208) show that the coefficients $\grave{k}_{x1}$ can assume zero or negative values or become unbounded under conditions involving little or no change in the phase hydrodynamics and system physical properties. Clearly such behaviour would defy correlation of the traditional kind (e.g. Chilton-Colburn j-factor correlation). A similar conclusion can be drawn for component 2. The pseudo-binary mass transfer coefficient for component 3, $\dot{k}_{x3}$, will assume values intermediate between those of components 1 and 2 when α has a positive value. When α is negative, $\dot{k}_{x3}$, assumes a value outside the range between $\dot{k}_{x1}$ and $\dot{k}_{x2}$. When $\alpha \simeq -1$, $\dot{k}_{x3}$ is unbounded

$$\dot{k}_{x3} \rightarrow \pm \infty \tag{209}$$

The conclusion regarding the unsuitability of the $\dot{k}_{xi}$ for describing ternary transport behaviour may be applied to systems of more than three components with even more conviction.

VIII. SIMULTANEOUS MASS AND ENERGY TRANSFER

Many processes such as distillation, condensation and evaporation involve simultaneous transfer of mass and energy across fluid–fluid interfaces. The presence of a temperature gradient in a multicomponent system introduces two additional complications: (i) variations in physical, thermodynamic and transport properties due to differences in temperature and (ii) large temperature gradients may give rise to material fluxes (thermal diffusion). The property variations due to temperature differences are taken care of quite simply by introducing temperature dependent property functions or by use of suitably averaged properties, as is commonly done; the basic mass transfer analysis remains essentially unchanged. The second complication arising out of 'coupling' between mass and energy transfer may have more important ramifications.

The interactions between thermal and mass fluxes have long been recognized. Much effort has been devoted to the study of thermal diffusion and many excellent reviews are available on the subject (Grew and Ibbs, 1962; Grew, 1969). Its practical application has been highlighted by the successful application of a thermal diffusion process to the separation of isotopes (Glasstone, 1958). Strong coupling effects may also be found in other physical processes involving steep temperature gradients, such as those involved in ablation cooling during rocket re-entry and in zone metal refining. The inverse Dufour effect, production of a heat flux due to concentration gradients, has received little attention in the literature, partly due to difficulties in experimentation (see, however, Green, 1968).

The diagonalization procedure of Toor and Stewart and Prober may be used to obtain the temperatures and composition profiles for coupled diffusion and heat conduction within a single fluid phase (DeLancey, 1967; DeLancey and Chiang, 1968; DeLancey and Chiang, 1970; DeLancey, 1972). Experimental evidence obtained at the University of Manchester for non-isothermal distillation (Tavana, 1973) and for non-isothermal absorption (Danesh, 1973; Onal, 1974) has shown that interphase thermo-transfer effects are at most small for most chemical engineering operations of practical interest. We therefore exclude possibilities of coupling between heat and mass transfer in the treatment below.

VIII.1. Energy Fluxes, Temperature Driving Forces, Heat Transfer Coefficients

For transfer within a single fluid phase, the differential energy balance provides the additional physical law necessary to determine the temperature profiles. This balance relation may be written in various forms (BSL; Slattery, 1972). Two useful forms of the equation, assuming mechanical equilibrium, are:

$$\frac{\partial \left\{\sum_{i=1}^{n} c_i \bar{H}_i\right\}}{\partial t} = - \nabla \cdot \left[\mathbf{q} + \sum_{i=1}^{n} \bar{H}_i \mathbf{N}_i\right] \tag{210}$$

and

$$\frac{\partial (c\, C_p T)}{\partial t} = - \nabla \cdot \mathbf{q} - \nabla \cdot (c\, C_p T \mathbf{u}) - \sum_{i=1}^{n} \mathbf{J}_i \cdot \nabla \bar{H}_i \tag{211}$$

$\mathbf{q}$ is the conductive heat flux and is adequately represented by Fourier's law

$$\mathbf{q} = - k_T \nabla T \tag{212}$$

where k_T is the thermal conductivity of the fluid mixture. $\mathbf{q}$ plays a role analogous to the diffusion fluxes $\mathbf{J}_i$ for mass transfer. In addition to the purely conductive heat flux $\mathbf{q}$ there is a contribution due to the enthalpies of the transferring species and the total energy flux is given by

$$\mathbf{E} = \mathbf{q} + \sum_{i=1}^{n} \bar{H}_i \mathbf{N}_i \tag{213}$$

$\mathbf{E}$ plays a role in energy transfer analogous to the total molar fluxes $\mathbf{N}_i$ for mass transfer. Thus under steady-state conditions, the total energy flux $\mathbf{E}$ is invariant along the transfer path (cf. equation (210)).

We shall illustrate the procedure for obtaining the temperature profiles and heat fluxes by considering a simple example: steady-state unidirectional heat and n-component mass transfer in the gaseous phase. It is assumed that the temperatures (and compositions) of either end of the transfer path, of thickness δ, are known and remain constant during the transfer process. Thus the boundary conditions are:

$$\text{at } z = 0, \quad T = T_0 \tag{214}$$

$$\text{at } z = \delta, \quad T = T_\delta$$

with analogous boundary conditions for compositions, equation (69). The determination of the composition profiles and molar total diffusive fluxes has been considered in III.1; with suitably averaged temperature properties the mass transfer analysis would remain unchanged. We therefore consider the z-invariant fluxes $\mathbf{N}_i$ to be known for the purposes of the ensuing analysis.

In proceeding to obtain the temperature profiles, it is convenient to define the following parameters:

(i) a dimensionless distance within the film

$$\eta = z/\delta \tag{215}$$

(ii) 'zero flux' heat transfer coefficient in the gaseous phase

$$h_y = k_T/\delta \tag{216}$$

With a suitably averaged value for the mixture thermal conductivity, the coefficient h_y may be considered constant along η.

(iii) dimensionless heat transfer rate factor

$$\varepsilon = \frac{\sum_{i=1}^{n} C_{pi}^{y} N_i}{h_y} \tag{217}$$

where C_{pi}^{y} is the molar heat capacity of the species i in the gaseous phase. Again, with suitably temperature averaged values, the factor ε can be considered to be η-invariant.

If the gaseous phase is considered to be an ideal mixture and if the reference state for calculation of the enthalpies is chosen as pure gas at the temperature T_δ, then we have

$$\bar{H}_i^y = C_{pi}^{y}(T - T_\delta) \tag{218}$$

and equation (210) simplifies to

$$E = -h_y \frac{dT}{d\eta} + h_y \varepsilon (T - T_\delta) = E_0 = E_\delta = \text{constant} \tag{219}$$

Equation (219) may be integrated for the boundary conditions (214) to give the temperature profiles as

$$\frac{T - T_0}{T_\delta - T_0} = \frac{e^{\varepsilon\eta} - 1}{e^{\varepsilon} - 1} \tag{220}$$

The conductive heat flux q_0^y may be obtained by differentiating (220) to give

$$q_0^y = -h_y \frac{dT}{d\eta}\bigg|_{\eta=0} = h_y \frac{\varepsilon}{e^{\varepsilon} - 1}(T_0 - T_\delta) \tag{221}$$

The total flux E may be obtained as

$$E = E_0 = E_\delta = q_0^y + \sum_{i=1}^{n} N_i C_{pi}^{y}(T_0 - T_\delta) \tag{222}$$

The above steady-state analysis forms the basis of the film theory estimation of the heat transfer coefficient under conditions of finite mass transfer rates. Thus if we define a finite flux heat transfer coefficient $h_y^\bullet$ by

$$q_0^y = h_y^\bullet (T_0 - T_\delta) \tag{223}$$

we see that the finite flux coefficient $h_y^\bullet$ is related to the zero flux value h_y by

$$h_y^\bullet = h_y \frac{\varepsilon}{e^\varepsilon - 1} \tag{224}$$

The factor $\varepsilon/(\exp\varepsilon - 1)$ gives the effect of finite mass transfer rates on the heat transfer coefficient h_y. This correction arises due to the alteration of the temperature profiles due to convective enthalpy transfers. In the limit of vanishing mass transfer rates ($N_i \rightarrow 0$), the temperature profiles are linear:

$$\frac{T - T_0}{T_\delta - T_0} = \eta \qquad |N_i \rightarrow 0| \tag{225}$$

When there is net movement of mass from $z = 0$ to $z = \delta$, then ε is positive and the factor $\varepsilon/(\exp\varepsilon - 1)$ is less than unity; the finite flux heat transfer coefficient $h_y^\bullet < h_y$. On the other hand if there is net movement of mass from $z = \delta$ to $z = 0$, the correction factor is greater than unity and $h_y^\bullet > h_y$.

The mass transfer corrections for other transfer models (penetration and boundary layer theories) is discussed in BSL for the case of two-component systems; extensions of the analyses to the general n-component case is straightforward as demonstrated above for the film theory case.

Let us now consider *inter*phase energy transfer. With assumptions parallel to those in V.1, it can be shown that an energy balance at the interface between two fluid phases shows that the normal components of the energy flux **E**,

$$E_b^y = E^y = E^x = E_b^x = E \tag{226}$$

are phase invariants. In most applications of chemical engineering interest we neglect the terms in the normal energy flux expressing the rate of transfer of kinetic energy and the rate of doing work by the surface frictional stresses. With this simplification, the invariant energy flux may be written, for phase 'x',

$$E^x = q^x + \sum_{i=1}^{n} \bar{H}_i^x N_i \tag{227}$$

with a parallel relation for phase 'y'.

In practical situations transfer between phases takes place by combined molecular and turbulent eddy mechanisms. It is common in practice to define heat transfer coefficiens which reflect the combined facility for transfer offered by the phase under consideration. Thus we may write for the bulk conductive fluxes

$$q_b^x = h_{xb}^\bullet (T_I - T_b) \tag{228}$$

The finite flux coefficient $h_{xb}^\bullet$ may be obtained from the zero flux coefficient h_{xb} by use of hydrodynamic mass transfer models. The zero flux coefficient is to be estimated from heat transfer correlations for the particular equipment and operating conditions. The film theory correction described above is adequate for most practical cases.

IX. ADDITION OF PHASE RESISTANCES FOR NON-ISOTHERMAL MULTICOMPONENT MASS TRANSFER

In the preceeding analysis we have considered methods for estimating mass and heat transfer coefficients in either phase during heat and mass transfer. In the calculation of the transfer rates, it was assumed that the interfacial compositions and temperatures were known. In practice each of the contiguous fluid phases will offer resistance to the transfer process and so may the interface itself, in some cases. It is useful to define, and calculate, overall mass and heat transfer coefficients which depict the overall resistance to transfer offered by the fluid–fluid system; the overall resistance will determine the system behaviour. Addition of mass transfer resistances for binary systems is discussed widely in the literature (BSL; Sherwood, Pigford and Wilke, 1975); here we consider extensions of conventional treatments to the multicomponent case (Krishna and Standart, 1976c, Toor, 1964). The interfacial resistance is ignored in the present analysis.

We consider a vapour–liquid system with n components in either phase and maintained at constant pressure. If we assume phase equilibrium at the interface itself, there are $n-1$ intensive interfacial state conditions, corresponding to the thermodynamic degrees of freedom, to be determined. It is convenient to choose the $n-1$ mole fractions x_{iI} as the independent state variables. The interfacial temperature and the $n-1$ interfacial vapour compositions y_{iI} will be determined by the vapour–liquid equilibrium relationship.

If the vapour–liquid equilibrium relationship is linearized over the range of compositions in passing from the bulk (b) to the interfacial (I) conditions we can write at the interface for isobaric conditions

$$(y_I) = [M]\,(x_I) + (b) \tag{229}$$

where $[M]$ is the matrix of equilibrium constants with elements

$$M_{ij} = \partial y_i^* / \partial x_j, \qquad i,j = 1,2,\ldots n-1 \tag{230}$$

and is diagonal only for thermodynamically ideal mixtures. (b) is a column matrix of 'intercepts'. For evaluation of M_{ij} see Krishna (1979b).

If we wish to combine mass transfer driving forces and resistances of each phase, we must require that at least one phase be saturated; this is necessary for eliminating the partial driving force for that phase. The assumption concerning saturation is implicit in conventional approaches to the binary transport problem and will be used here for the multicomponent case. Here we assume that the liquid phase is saturated; this allows us to calculate the composition of the vapour which would be in equilibrium with the bulk liquid phase as

$$(y^*) = [M]\,(x_b) + (b) \tag{231}$$

If we adopt the sign convention that transfer of species i from the vapour to the liquid phase is considered positive, we may write the bulk diffusion flux in the vapour phase as (cf. equation (173))

$$(J^y_b) = [k^\bullet_{yb}]\,(y_b - y_I) \tag{232}$$

where $[k^\bullet_{yb}]$ is the $n-1 \times n-1$ square matrix of (partial) vapour phase mass transfer coefficients. The calculation of the total fluxes N_i, which are phase invariant, requires an additional determinancy condition as discussed in V.4. If the determinancy in the vapour phase is described in terms of a bootstrap solution matrix $[\beta^y]$, we may write the total fluxes as

$$(N) = [\beta^y]\,(J^y_b) = [\beta^y]\,[k^\bullet_{yb}]\,(y_b - y_I) = [W_y]\,(y_b - y_I) \tag{233}$$

where we have used the matrix of total transfer coefficients in the vapour phase, $[W_y]$, defined by

$$[W_y] = [\beta^y]\,[k^\bullet_{yb}] \tag{234}$$

As an alternative to (232) we may define a matrix of overall vapour phase mass transfer coefficients using

$$(J^y_b) = [K^\bullet_{0yb}]\,(y_b - y^*) \tag{235}$$

and the total fluxes being obtained in terms of an overall matrix of total mass transfer coefficients

$$(N) = [W_{0y}]\,(y_b - y^*) \tag{236}$$

where

$$[W_{0y}] = [\beta^y]\,[K^\bullet_{0yb}] \tag{237}$$

The bulk diffusion fluxes in the liquid phase may be written as

$$(J^x_b) = [k^\bullet_{xb}]\,(x_I - x_b) \tag{238}$$

with the total fluxes given by

$$(N) = [W_x]\,(x_I - x_b) \tag{239}$$

where the total transfer coefficients in the liquid phase are obtained in terms of the bootstrap solution for the liquid phase

$$[W_x] = [\beta^x]\,[k^\bullet_{xb}] \tag{240}$$

From equation (236) the overall vapour phase driving force can be written as

$$(y_b - y^*) = [W_{0y}]^{-1}\,(N) \tag{241}$$

and from equation (233) we have

$$(y_b - y_I) = [W_y]^{-1} (N) \tag{242}$$

The partial driving forces in the liquid phase are obtained from (239) as

$$(x_I - x_b) = [W_x]^{-1} (N) \tag{243}$$

Premultiplication of both sides of equation (242) by $[M]$ yields in view of equations (229) and (231)

$$(y_I - y^*) = [M]\,[W_x]^{-1} (N) \tag{244}$$

Since the $n-1$ total fluxes N_i ($= N_i^y = N_i^x$) are all independent we may combine equations (241), (242) and (244) to give the addition of resistances 'formula' for multicomponent systems:

$$[W_{0y}]^{-1} = [W_y]^{-1} + [M]\,[W_x]^{-1} \tag{245}$$

which is the proper matrix generalization of the classical addition of resistances for binary mass transfer (Krishna and Standart, 1976c).

For the special case of equimolar counter transfer the bootstrap solution matrices in either phase reduce to identity matrices and equation (245) reduces to

$$[K^\bullet_{0yb}]^{-1} = [k^\bullet_{yb}]^{-1} + [M]\,[k^\bullet_{xb}]^{-1} \tag{246}$$

which is the relation obtained earlier by Toor (1964).

It is clear from equation (245) that the requirement that the overall matrix $[W_{0y}]$ be diagonal is very stringent; it requires that the matrices $[k^\bullet_{yb}]$, $[\beta^y]$, $[k^\bullet_{xb}]$, $[\beta^x]$ and $[M]$ be severally diagonal. The general conclusion to be drawn here is that the multicomponent interphase mass transfer must always be described by non-diagonal matrices of transfer coefficients.

It is also difficult for a multicomponent system to state whether one or other phase 'controls' the transfer behaviour. For non-ideal mixtures the element M_{ij} could dramatically change magnitude and possibly sign in the same column with slightly varying intensive properties. The mass transfer control could then shift from one phase to the other.

Turning now to the heat transfer analysis, we have the partial heat transfer coefficients in the vapour and liquid phases:

$$q_b^y = h^\bullet_{yb} (T_{by} - T_I); \; q_b^x = h^\bullet_{xb} (T_I - T_{bx}) \tag{247}$$

and we may also *define* an overall heat transfer coefficient in the vapour phase by $q_b^y = h^\bullet_{0yb} (T_{by} - T_{bx})$, but such a coefficient has no practical utility, except in the absence of mass transfer.

X. PRACTICAL APPLICATIONS IN SEPARATION PROCESSES

We now consider applications of the formalisms developed so far to some practical separation processes.

X.1 MULTICOMPONENT DISTILLATION IN A TRAY COLUMN

Distillation of multicomponent mixtures in tray columns is an operation widespread in the process industries. Most experimental research work on distillation reported in the literature has been concerned with simple two component systems, whereas most practical systems have at least three components. As we have seen in this review the transfer characteristics of systems with three or more species are quite different from that exhibited by binary systems; in particular it is possible for a multicomponent system to experience the three interaction phenomena described in Section VI. We consider here the simple example of determining the Murphree point efficiencies for distillation of a ternary mixture in a tray column. The liquid on the tray is assumed to be well mixed and the vapour is assumed to be in plug flow through the dispersion on the tray. Our treatment here essentially follows Toor (1964a).

For a narrow vertical section in the foam on the tray, the component material balance may be written as

$$\frac{dG_i}{dz} = -N_i a \mathcal{A}_T, \qquad i = 1,2,3 \tag{248}$$

Here G_i is the molar flow rate of the species i in the vapour phase; Z is the distance along the vertical direction; N_i is the molar flux of species i, considered positive for transfer from the bulk vapour to the bulk liquid phase; a is the interfacial area per unit volume of dispersion; $\mathcal{A}_T$ is the element of tray area for the vertical slice under consideration.

The molar flow rate of the vapour mixture may be obtained on summing (248) over the three species and we obtain

$$\frac{dG_t}{dZ} = -N_t a \mathcal{A}_T \tag{249}$$

The differential material balance may also be written in terms of the bulk vapour phase mole fractions y_{ib} $(= G_i/G_t)$ and we obtain in view of equation (166)

$$G_t \frac{dy_{ib}}{dZ} = -J^V_{ib} a \mathcal{A}_T, \qquad i = 1,2,3 \tag{250}$$

Since only two of the equations (250) are independent we may re-write (250) conveniently in 2-dimensional matrix notation as

$$\frac{d(y_b)}{d\xi} = -\frac{(J^V_b) a V}{G_t} \tag{251}$$

where we denote V as the total volume of dispersion in the vertical section and ξ is the fractional height of dispersion on the tray.

Let x_{ib} denote the bulk liquid composition in the section and y_i^* denote the composition of the vapour in equilibrium with the bulk liquid compositions x_{ib}. Since the liquid is assumed to be well mixed vertically, the compositions x_{ib} and y_i^* will be constant along the vertical slice. Using overall vapour phase composition driving forces and overall matrix of transfer coefficients, the constitutive relations for the bulk diffusion fluxes J_{ib}^V take the form of equation (235). Introducing these rate relations in equation (251) we obtain

$$\frac{d(y_b)}{d\xi} = -\frac{[K^\bullet_{0yb}]\, a\, V}{G_t}\,(y_b - y^*) \tag{252}$$

It is convenient to define a matrix of overall number of vapour phase transfer units,

$$[NTU_{0y}] = \frac{[K^\bullet_{0yb}]\, a\, V}{G_t} \tag{253}$$

Since most mass transfer correlations predict that the vapour phase mass transfer coefficients to vary with $G_t^{0.8}$, we may expect the elements of the matrix $[NTU_{0y}]$ to vary weakly with the hydrodynamics. Another advantage of the definition (252) is that the matrix $[NTU_{0y}]$ includes the usually unknown interfacial area a.

If we assume that the elements of the matrix $[NTU_{0y}]$ remain constant along the vertical section, we may integrate the differential equation

$$\frac{d(y_b)}{d\xi} = -\,[NTU_{0y}]\,(y_b - y^*) \tag{254}$$

for the boundary conditions

$$\begin{aligned} &\text{at } \xi = 0,\ (y_b) = (y_b)_E;\ (\Delta y) = (\Delta y)_E = (y_b)_E - (y^*) \\ &\text{at } \xi = 1,\ (y_b) = (y_b)_L;\ (\Delta y) = (\Delta y)_L = (y_b)_L - (y^*) \end{aligned} \tag{255}$$

to obtain

$$(\Delta y)_L = \exp\{-[NTU_{0y}]\}\,(\Delta y)_E \tag{256}$$

It is convenient for future discussions to define the matrix $[\mathcal{G}]$ as

$$[\mathcal{G}] = \exp\{-[NTU_{0y}]\} \tag{257}$$

and so the equation (256) may be written explicitly for the components 1 and 2 as

$$\Delta y_{1L} = \mathcal{G}_{11}\Delta y_{1E} + \mathcal{G}_{12}\Delta y_{2E} \tag{258}$$

$$\Delta y_{2L} = \mathcal{G}_{21}\Delta y_{1E} + \mathcal{G}_{22}\Delta y_{2E}$$

Now, the Murphree point efficiency for component i is given by

$$\grave{E}_{0yi} = \frac{y_{ibE} - y_{ibL}}{y_{ibE} - y_i^*} \qquad i = 1,2,3 \tag{260}$$

If we define α as the ratio of driving forces

$$\alpha = \frac{\Delta y_{1E}}{\Delta y_{2E}} = \frac{y_{1bE} - y_1^*}{y_{2bE} - y_2^*} \tag{261}$$

we may write the component efficiencies for components 1 and 2 in view of equations (258) and (259) as

$$\grave{E}_{0y1} = 1 - \mathcal{G}_{11} - \mathcal{G}_{12}/\alpha \tag{262}$$

$$\grave{E}_{0y2} = 1 - \mathcal{G}_{22} - \mathcal{G}_{21}\alpha \tag{263}$$

with the component 3 efficiency given by

$$\grave{E}_{0y3} = \frac{\alpha\grave{E}_{0y1} + \grave{E}_{0y2}}{\alpha + 1} \tag{264}$$

Since the cross coefficients of $[k_{yb}^{\bullet}]$ will be generally non-zero, the coefficients $\mathcal{G}_{12}$ and $\mathcal{G}_{21}$ will also be non-zero. Examination of equations (262)–(264) shows that the efficiencies of the three components 1,2 and 3 will all be unequal. This is in contrast to a binary system which is characterised by only one efficiency, equal for both components in the mixture. The above equations also show that the component efficiency values for a ternary mixture will depend on the ratio of driving forces α.

Let us assume that the component numbering has been chosen such that the cross-coefficients $K_{0yb12}^{\bullet}$ and $K_{0yb21}^{\bullet}$ are positive; it has been shown in section VI that for this purpose we need to choose the numbering such that the transfer facility for component 1 in 2 is smallest (cf. equations (182) and (183)). With this choice of numbering, the elements $\mathcal{G}_{12}$ and $\mathcal{G}_{21}$ will be negative (cf. equation (257)). The main coefficients $\mathcal{G}_{11}$ and $\mathcal{G}_{22}$ will have the same sign as the main elements $K_{0yb11}^{\bullet}$ and $K_{0yb22}^{\bullet}$ and will therefore be always positive.

When α assumes a large and positive value, we see from equation (263) that the component 2 efficiency $\grave{E}_{0y2}$ may assume values exceeding unity. On the other hand, when α assumes a large but negative value, equation (262) shows that $\grave{E}_{0y1}$ may assume negative values. When $\alpha \simeq -1$, the component 3 efficiency, $\grave{E}_{0y3} \rightarrow \pm\infty$. It must be remembered that for a binary system, the component values of the point efficiencies always lie between 0 and 1. The bizarre behaviour exhibited by the ternary system, typical of multicomponent systems, is due to diffusional interaction phenomena. The Murphree point efficiency for a multi-component system would therefore defy simple correlation with the system hydrodynamics and transport properties (cf. discussion on the unsuitability of the $\grave{k}_{xi}$ in section VII.).

For highly non-ideal mixtures, the differences in the component efficiencies will be large, such differences increasing with large magnitudes of α. On the other hand for mixtures made up of similar components (e.g. close boiling hydrocarbon mixtures) the diffusional interaction effects will be small and the component efficiencies will be close to one another. These conclusions are confirmed by available experimental evidence (Cermak, 1970; Chernykh, Malyusov and Mafeev, 1971; Diener and Gerster, 1968; Free and Hutchison, 1960; Gelbin, 1965; Goldberg, Serafimov, Boyarchuk and L'vov, 1968; Haselden and Thorogood, 1964; Hutchison and Lusis, 1968; Konstantinov and Nikolaev, 1964; Martinez, 1975; Miskin, Ozalp and Ellis, 1972; Nord, 1946; Shporin and Nikolaev, 1968; Vertuzaev, Lyskov and Ganenok, 1971; Vogelpohl, 1972, 1979; Young and Weber, 1972).

In order to demonstrate the magnitude of the interaction effects possible during distillation of non-ideal mixtures, we have presented in Table 1 some experimental data obtained at the University of Manchester by Martinez (1975) and Sreedhar (1975) for distillation of ethanol (1)–*tert* butanol (2)–water (3) in a 3-inch diameter sieve tray column. The experimental conditions were maintained such that the assumption of perfectly mixed liquid on the tray was valid. For the system studied, the transfer

TABLE 1

Typical Experimental Results for Distillation of ethanol (1)–*tert* butanol (2)–water (3) in a 3-inch diameter Sieve Tray Column—Murphree Efficiencies for Individual Components. Measurements made by Martinez (prefixed M) and Sreedhar (S) under identical hydrodynamic conditions for each run.

Run No.	α	$\dot{E}_{0yi}$	$\dot{E}_{0y2}$	$\dot{E}_{0y3}$
S11A	0.2304	0.0699	0.6779	0.5638
M5	0.2080	0.0578	0.7137	0.6010
M7	0.4264	0.2039	0.7766	0.6058
M22	0.8489	0.5671	0.7098	0.6443
S11C	19.17	0.6491	2.0019	0.7162
M3	9.9	0.6169	1.3577	0.6848
M6	11.2	0.6455	1.2058	0.6906
M9	11.7	0.5144	2.9244	0.7092
M34	9.1	0.4463	1.0491	0.5050
M41	32.4	0.4433	1.5891	0.4780
M47	85.7	0.4605	5.2700	0.5170
M49	1.1289	0.5331	1.0735	0.7865
M40	−7.65	0.4811	0.1853	0.5256
M46	−26.8	0.3546	−2.94	0.4800
M12	−60.8	0.4790	−1.2888	0.5095
M1	−237	0.6509	−27.9	0.7202

coefficient of ethanol in *tert* butanol is the smallest of the values of the three binary pairs in both the liquid and vapour phases. The coefficients $\mathcal{G}_{12}$ and $\mathcal{G}_{21}$ will there be negative. The values of the component efficiencies E_{0yi} listed in Table 1 will be seen to be explainable in terms of equations (262)–(264), thus confirming the mass transfer formulations developed here (see Krishna et al, 1977d).

Further experimental confirmation of the importance of diffusional interactions in multicomponent distillation is obtained from the experimental work reported by Vogelpohl (1979) for the system acetone–methanol–water and methanol–isopropanol–water.

From a practical point of view, the overall transfer coefficient matrix $[K^{\bullet}_{0yb}]$ can be calculated from information on the partial transfer coefficients as outlined in section IX. and the overall number of vapour phase transfer units calculated from equation (253). This provides a method of predicting the component efficiencies E_{0yi} which information is required for design purposes.

The design engineer who assumes equal efficiencies may suffer a severe embarassment as a result of neglecting cross (or coupling) effects as this may lead to a severe underdesign as shown in an interesting theoretical study made by Toor and Burchard (1960). For systems under complete vapour phase mass transfer control, equations were developed based on the generalized driving force pseudo-binary approach, mentioned earlier in section VII, for the effects of diffusional interactions among the components on their respective plate efficiency. A design calculation was made for the separation of methanol from isopropanol and water. For the hypothetical case in which the binary efficiencies were assumed to be 40%, consideration of interactions gave a column requiring 117 plates compared with 84 plates for the case where diffusional interactions are negligible.

X.2 Multicomponent Distillation in Continuous Contact Equipment

For distillation of multicomponent mixtures in continuous columns (packed or wetted-wall), the treatment is essentially the same as considered in X.1. Thus the differential equation describing the composition variations along the height of the column (ξ representing the fractional height) may be derived as

$$\frac{d(y_b)}{d\xi} = -\,[NTU_{0y}]\,(y_b - y^*) \tag{265}$$

where now $[NTU_{0y}]$, the matrix of overall vapour phase number of transfer units, is given by

$$[NTU_{0y}] = \frac{[K^{\bullet}_{0yb}]\ \mathrm{a\ A\ Z}}{G_t} \tag{266}$$

where a is the interfacial area per unit 'packed' volume; A is the cross sectional area of the column; Z is the total height of the column. (y^*), the equilibrium vapour compositions, vary along the column height.

The integrations of equation (265) must be carried out in a stepwise manner either to obtain the separation achievable in a given column or to find the height required for a given separation.

More conventionally, we may *define* the number of transfer units for each of the species in the mixture by

$$N\grave{T}U_{0yi} = \int_{\xi=1}^{\xi=0} \frac{dy_{ib}}{y_{ib} - y_i^*} \qquad i = 1,2,\ldots n \tag{267}$$

and therefore the heights of transfer units, characterizing the separation capability of the column, will be given as

$$H\grave{T}U_{0yi} = Z/N\grave{T}U_{0yi}, \qquad i = 1,2,\ldots n \tag{268}$$

For distillation of non-ideal multicomponent mixtures the pseudo-binary heights of transfer units, $H\grave{T}U_{0yi}$, will be all unequal (this conclusion is analogous to the conclusion reached for the Murphree efficiencies $\grave{E}_{0yi}$). On the other hand for ideal mixtures made up of species of similar nature the $H\grave{T}U_{0yi}$ will be close to one another. Available experimental data confirm these conclusions (Free and Hutchison, 1960; Hutchison and Lusis, 1968; Qureshi and Smith, 1958; Rahman, 1975; Salomo, 1976).

Experiments were carried out at the University of Manchester for distillation of the system ethanol (1)–*tert* butanol (2)–water (3) in a 2-inch diameter wetted-wall column with a test section of height 1 m. The pseudo-binary number of transfer units $N\grave{T}U_{0yi}$ for the three species were calculated using equation (267). Some typical values, obtained by Rahman (1975) and Salomo (1976), are shown in Table 2. The dependence of the pseudo-binary $N\grave{T}U_{0yi}$ on the ratio of driving forces α, given by

TABLE 2

Typical Experimental Results for Distillation of ethanol (1)–*tert* butanol (2)–water (3) in a 2-inch diameter Wetted-Wall Column—Pseudo-Binary Numbers of Transfer Units for Individual Components. Measurements made by Rahman (prefixed R) and Salomo (prefixed S) under almost identical hydrodynamic conditions for each run.

Run No.	α	$N\grave{T}U_{0y1}$	$N\grave{T}U_{0y2}$	$N\grave{T}U_{0y3}$
S1	0.4494	1.054	0.825	0.899
S17	0.2251	1.161	0.830	0.894
S18	0.2571	1.283	0.924	0.993
R3	0.2504	1.642	0.712	0.922
R4	0.4676	1.579	0.553	0.926
R11	0.2668	1.435	0.567	0.774
S20	1.7088	0.644	0.901	0.727
R6	1.4719	0.419	1.243	0.719

$$\alpha = \frac{(y_{1b} - y_1^*)_{\xi=0}}{(y_{2b} - y_2^*)_{\xi=0}} \tag{269}$$

can be explained if we consider that for a differential section the following relations hold

$$N\grave{T}U_{0y1} = NTU_{0y11} + NTU_{0y12}/\alpha \tag{270}$$

$$N\grave{T}U_{0y2} = NTU_{0y22} + NTU_{0y21}\,\alpha \tag{271}$$

$$N\grave{T}U_{0y3} = \frac{\alpha\, N\grave{T}U_{0y1} + N\grave{T}U_{0y2}}{\alpha + 1} \tag{272}$$

(these relations are analogous to equations (262)–(264)).

The pseudo-binary numbers of transfer units $N\grave{T}U_{0yi}$, or equivalently the pseudo-binary heights of transfer units $H\grave{T}U_{0yi}$, show odd driving force dependencies and are therefore unsuitable for use as correlation parameters. An analogous conclusion was reached for the pseudo-binary mass transfer coefficients (section VII). The correct representation of the mass transfer behaviour during multicomponent distillation is obtained by use of the matrices of transfer coefficients, $[k^\bullet_{yb}]$, $[k^\bullet_{xb}]$ and the matrix of overall number of transport units $[NTU_{0y}]$.

Sandall and Dribicka (1979) give further experimental evidence of the validity of the mass transfer model discussed here.

X.3 *Thermal Effects in Distillation*

The assumption of equimolar counter-transfer, $N_t = 0$, is implicit in most chemical engineering textbook calculations of the interfacial rates of transfer during distillation. The basis of this assumption is the fact that the molar heats of vaporization of most chemical compounds are very close to one another and for distillation under adiabatic conditions of say methanol–water, the condensation of one mole of water vapour results in the evaporation of one mole of methanol. Since we have at our disposal the correct formalisms for the treatment of non-isothermal mass transport processes, we shall consider the validity of the assumption of equimolar counter transfer for multicomponent distillation; the treatment here is due to Krishna and Standart (1976d).

Consider any local position in a distillation equipment. Thus we have a vapour phase in contact with a liquid phase; heat and mass are transferred across the interface. We assume adiabatic conditions, justifiable in most practical cases. A material and energy balance at the interface leads to the requirement of continuity of mass, equation (163), and energy, equation (226). Writing the material fluxes in either phase in terms of the diffusive and convective contributions (cf. equation (166) we have

$$N_i = J^y_{ib} + y_{ib}N_t = J^x_{ib} + x_{ib}N_t, \quad i = 1,2,\ldots n-1 \tag{273}$$

where only the $n-1$ independent relations are considered. The appropriate rate relations for the diffusion fluxes are

$$(J_b^y) = [k_{yb}^{\bullet}]\,(y_b - y_I);\ (J_b^x) = [k_{xb}^{\bullet}]\,(x_I - x_b) \tag{274}$$

where we have adopted the convention that transfer from the vapour to the liquid phase is positive.

The energy balance at the interface may be expressed as

$$E = q_b^y + \sum_{i=1}^{n} \bar{H}_{ib}^y N_i = q_b^x + \sum_{i=1}^{n} \bar{H}_{ib}^x N_i \tag{275}$$

or

$$q_b^x - q_b^y = \sum_{i=1}^{n} (\bar{H}_{ib}^y - \bar{H}_{ib}^x)\,N_i \tag{276}$$

If we define the differences in the partial molar enthalpies in the vapour and liquid phases as λ_i,

$$\lambda_i = \bar{H}_{ib}^y - \bar{H}_{ib}^x, \qquad i = 1,2,\ldots n \tag{277}$$

and also define the parameters

$$\bar{\lambda}_y = \sum_{i=1}^{n} y_{ib}\lambda_i;\ \bar{\lambda}_x = \sum_{i=1}^{n} x_{ib}\lambda_i \tag{278}$$

we may write equation (276) in view of equations (273) as

$$q_b^x - q_b^y = \sum_{i=1}^{n-1} (\lambda_i - \lambda_n)\,J_{ib}^y + \bar{\lambda}_y N_t = \sum_{i=1}^{n-1} (\lambda_i - \lambda_n)\,J_{ib}^x + \lambda_x\,N_t \tag{279}$$

The conductive heat fluxes in (279) are given by the rate relations

$$q_b^x = h_{xb}^{\bullet}\,(T_I - T_{xb});\ q_b^y = h_{yb}^{\bullet}\,(T_{yb} - T_I) \tag{280}$$

If we assume that equilibrium prevails at the interface, there are *n*−*1* of interfacial intensive state conditions (x_{iI}, y_{iI}, T_I) which have to be determined. The *n*−*1* relations which allow this determination are obtained from equations (273) and (279) as

$$N_t = -\frac{J_{ib}^x - J_{ib}^y}{x_{ib} - y_{ib}} = \frac{q_b^x - q_b^y}{\bar{\lambda}_y} - \frac{\sum_{k=1}^{n-1} (\lambda_k - \lambda_n)\,J_{kb}^y}{\bar{\lambda}_y}, \qquad i = 1,2,\ldots n-1 \tag{281}$$

with a similar expression in terms of λ_x and $\mathbf{J}_{kb}^x$. Once the unknown interfacial parameters have been determined from (281) and the equilibrium relationship at the interface, the interfacial mass transfer rates may be obtained from equations (273) and (281) as

$$N_i = (1 - \Lambda_i y_{ib})\,\mathbf{J}_{ib}^y - y_{ib} \sum_{\substack{k=1 \\ k\neq i}}^{n-1} \Lambda_k\,J_{kb}^y + y_{ib}\,\frac{\Delta q}{\bar{\lambda}_y}, \qquad i = 1,2,\ldots n-1 \tag{282}$$

where we have defined the parameters

$$\Lambda_k = (\lambda_k - \lambda_n)/\bar{\lambda}_y; \quad \Delta q = q_b^x - q_b^y \tag{283}$$

Equations (282), (283) allow the calculation of the interfacial transfer rates without making the assumption of equimolar counter-transfer. We may write (282) in compact $n-1$ dimensional matrix notation as

$$(N) = [\beta^y]\,(J_b^y) + (y_b)\,\frac{\Delta q}{\bar{\lambda}_y} \tag{284}$$

where the elements of the 'bootstrap' solution matrix $[\beta^y]$ are given by

$$\beta_{ik}^y = \delta_{ik} - y_{ib}\Lambda_k, \qquad i,k = 1,2,\ldots n-1 \tag{285}$$

An expression analogous to (284) may be written for the liquid phase. It is interesting to compare equations (177) and (285) which show the generality of the bootstrap solution analysis considered in V.4.

The requirement of equimolar counter-transfer,

$$N_t = 0 \tag{286}$$

will be met if the following two conditions are satisfied:

$$\text{(i)}\ \Delta q = 0 \tag{287}$$

and

$$\text{(ii)}\ \lambda_i = \lambda_n, \qquad i = 1,2,\ldots n-1 \tag{288}$$

The difference between the conductive heat fluxes in the liquid and vapour phases can only vanish if these fluxes fortuitously cancel each other; we cannot expect (287) to represent a general, even common, result. The parameters λ_i, defined by equation (277), correspond roughly to molar heats of vaporization; their values will be close to one another but not identical. Let us now consider the consequences of small differences between the λ_i values. For purposes of illustration we take the example of a ternary mixture and assume that as an approximation (287) holds. Further, we take the following values for the parameters Λ_i:

$$\Lambda_1 = 0.1; \quad \Lambda_2 = 0.1 \tag{289}$$

allowing (typically) only 10% differences between the λ_i. The net mixture flux N_t is obtained from equation (281) as

$$N_t = 0.1\, J_{1b}^y + 0.1\, J_{2b}^y \tag{290}$$

For a ternary system the diffusion fluxes J'_{1b} and J'_{2b} are both independent and may differ by an order of magnitude. It is conceivable that we may have

$$J'_{2b} = 5\,J'_{1b} \tag{291}$$

and therefore from (290) we have the net mixture flux

$$N_t = 0.6\,J'_{1b} \tag{292}$$

leading to

$$N_1 = J'_{1b} + y_{1b}N_t = (1 + 0.6\,y_{1b})\,J'_{1b} \tag{293}$$

If the composition y_{1b} is typically 0.33, it is easy to check from equations (286) and (293) that the assumption of equimolar counter-transfer would result in a 20% error in the calculation of N_1. Thus small 10% differences in λ_i may be enhanced in multicomponent systems. Such effects are not present to such a dramatic extent in binary systems because for this case we must necessarily have

$$J'_{1b} = -J'_{2b} \tag{294}$$

and there will be no enhancement of the differences in molar latent heats of vaporization. For binary systems (286) represents a fair approximation and this explains its widespread usage. However, for systems of three or more species large deviations from (286) may be experienced, thus firmly underlining the fundamental differences between the transport characteristics of binary and multicomponent systems. Further calculations on the effects of unequal molar heats of vaporization are given by Krishna (1977f).

X.4 Condensation of Vapour Mixtures

Condensation of vapour mixtures is an operation of great significance in the process industries. The term vapour mixture covers a wide range of situations. One limit of this range is one in which all components have boiling points above the maximum coolant temperature; in this case the mixture can be totally condensed. The other limit is a mixture in which at least one component in the initial vapour stream has a boiling point lower than the minimum coolant temperature and is negligibly soluble in the liquid condensate formed by the remaining components and hence cannot be condensed at all. An intermediate case of some importance is typified by a mixture of light hydrocarbons, in which the lightest members often cannot be condensed as pure components by the heavier components. In each of the three cases, the vapour mixture may form a partially or totally immiscible condensate.

The process of condensation involves simultaneous transfer of mass and energy between the condensing vapour and liquid streams. The heat lost by the vapour to the condensing liquid is further removed by the coolant across the tube wall. At any local position in the condenser, vertical or horizontal, the energy balance at the vapour–liquid interface will be given formally by equations (275)–(280).

If we neglect subcooling of the liquid condensate, the conductive heat flux in the condensed liquid film, q_b^x, will also equal the heat flux through the wall of the condenser and carried away by the coolant on the other side of the wall. Thus we may write

$$q_b^x = q^w = h_0(T_I - T_c) \tag{295}$$

where h_0 is the heat transfer coefficient incorporating the resistances of the condensed liquid film, wall and coolant.

The finite flux heat transfer coefficient in the vapour phase $h_{yb}^\bullet$ is related to the zero flux heat transfer coefficient h_y by (cf. equation (224))

$$h_{yb}^\bullet = h_y \frac{\varepsilon}{e^\varepsilon - 1} \tag{296}$$

with ε given by equation (217). The zero flux coefficient may be obtained from a j-factor correlation of the type

$$j_H = \frac{h_y A}{G_t \bar{c}_p^y} (Pr)^{2/3} = a\ (Re)^b \tag{297}$$

If we further assume that the vapour phase is an ideal mixture, the energy balance relation at the interface may be written in the final 'working' form as

$$\begin{aligned} q^w = h_0 (T_I - T_c) &= h_y \frac{\varepsilon}{e^\varepsilon - 1} (T_{yb} - T_I) + \sum_{i=1}^{n} C_{pi}^y N_i (T_{yb} - T_I) + \sum_{i=1}^{n} \Delta H_{vi} N_i \\ &= h_y \frac{\varepsilon\, e^\varepsilon}{e^\varepsilon - 1} (T_{yb} - T_I) + \sum_{i=1}^{n} \Delta H_{vi} N_i \end{aligned} \tag{298}$$

where ΔH_{vi} is the molar heat of vaporization of species i. Thus, given the conditions in the bulk vapour and coolant streams at any position in the condenser, the interfacial parameters (T_I, x_{iI}, y_{iI}) must satisfy the energy balance relation (298) as well as the material balance relations (273) with the rate relations (274). If we assume equilibrium at the interface, there will be $n-1$ unknown interfacial parameters to determine. The estimation of the mass transfer coefficient matrices $[k_{yb}^\bullet]$ and $[k_{xb}^\bullet]$ and the calculation of the transfer rates N_i have been considered in section V. Basically a simple trial and error procedure is involved at every stage in the calculations. These interfacial transfer rate calculations have to be combined with the overall material and energy balances along the condenser length to obtain the working design equations.

When the vapour phase contains two or three components, the general analysis simplifies considerably; we consider three simple cases below.

X.4.a Condensation of a Single Vapour in the Presence of an Inert Gas

The vapour species (1) has to diffuse through the inert gaseous species (2) to the vapour-liquid interface before it can condense and release its heat to the coolant. The total rate of transfer of species 2, $N_2 = 0$ and the rate of transfer of the vapour species 1 is given by equation (86) or alternatively by (87). The interfacial vapour composition y_{1I} is given by

$$y_{1I} = P^{\circ}_1 \, (T_I)/p_t \tag{299}$$

where $p^{\circ}_1 \, (T_I)$ is the vapour pressure of 1 at the temperature of the interface T_I; p_t is the total pressure prevailing in the condenser. There is thus only one $(n-1 = 2-1 = 1)$ interfacial paramater, namely the temperature T_I, to determine. The calculation procedure at any position is: (i) assume T_I, (ii) calculate y_{1I} from (299), (iii) estimate h_y and k_{y12} from j_H $(=j_D)$ correlations, (iv) calculate N_1 from (87), (v) from a knowledge of the coolant temperature T_c at the position under consideration, check that (298) is satisfied. If the balance of energy is not satisfied, a new value of T_I is assumed and steps (ii) to (v) repeated till convergence is obtained.

X.4.b Condensation of a Binary Vapour Mixture

Most design procedures for the condensation of a binary vapour mixture follow the classic analyses of Ackermann (1937) and Colburn and Drew (1937) which employ a 'film' model for the description of the transfer processes in the vapour phase. Strictly speaking, the calculation of the rates of mass transfer requires the knowledge of the mass transfer coefficient k_{x12} in the liquid phase. This requirement is circumvented in the Colburn and Drew analysis by assuming that the composition of the condensed liquid at the interface, x_{1I}, is determined by the relative rates of condensation of species 1 and 2, i.e.

$$x_{1I} = N_1/N_t = 1 - x_{2I} = 1 - N_2/N_t \tag{300}$$

From equation (170) it is clear that for (300) to hold it is implied that

$$\mathcal{J}_{1I} = 0; \quad k^{\bullet}_{xI12} = 0 \tag{301}$$

which would apply if the condensate film near the interface would be completely 'unmixed' with no diffusive transfer.

The composition of the vapour at the interface in equilibrium with the liquid is given by

$$y_{1I} = \frac{\gamma_1 \, x_{1I} \, p^{0}_1 \, (T_I)}{p_t} \, ; \; y_{2I} = 1 - y_{1I} \tag{302}$$

The molar rate of condensation of species i can be calculated from

$$N_1 = \frac{J^y_{1b}}{1 - y_{1b}/x_{1I}} = k^{\bullet}_{yb12} \frac{(y_{1b} - y_{1I})}{(1 - y_{1b}/x_{1I})} \;;\; N_2 = \frac{x_{2I}}{x_{1I}} N_1 \tag{303}$$

or equivalently using

$$N_1 = k_{y12}\, x_{1I} \ln \frac{1 - y_{1I}/x_{1I}}{1 - y_{1b}/x_{1I}} \;;\; N_2 = \frac{x_{2I}}{x_{1I}} N_1 \tag{304}$$

As in X.4.a, there is one unknown interfacial parameter to determine; this parameter is conveniently chosen as the interfacial temperature T_I. The trial and error procedure to be used at each interval in the condenser is as follows: (i) assume interface temperature T_I, (ii) calculate x_{1I} and y_{1I} from equilibrium data at system total pressure p_t; (iii) calculate N_1, N_2 from (303) or (304) in which the zero flux coefficient k_{y12} is estimated from an appropriate j_D correlation, (iv) check the energy balance relation (298). If the balance is satisfied we proceed to the next increment and the solution of overall material and energy balances; if the balance is not satisfied another temperature T_I is assumed and the steps (ii)–(iv) repeated till convergence is obtained on T_I. A Newton-Raphson procedure is appropriate for the iteration on T_I.

X.4.c Condensation of a Binary Vapour Mixture in the Presence of an Inert Gas

The analysis of this case is complicated due to the fact that the vapour phase is a ternary mixture and as has been noted in this review, there are possibilities of diffusional interactions in the vapour phase. Krishna and Panchal (1977b) developed a generalized Ackermann–Collburn and Drew type analysis for this case, based on multicomponent 'film' model of Krishna and Standart (1976a), discussed in III.1 and V.3. We summarize the analysis here.

For the case under consideration we have

$$N_3 = 0 \tag{305}$$

The transfer rates in the vapour phase N_1 and N_2 are given by equation (233) where the elements of the bootstrap solution matrix, $[\beta^y]$, are given by (cf. equations (75), (76) and (177))

$$\beta^y_{ik} = \delta_{ik} + y_{ib}/y_{3b}, \qquad i,k = 1,2 \tag{306}$$

The matrix of finite flux mass transfer coefficients $[k^{\bullet}_{yb}]$ is obtained from equations (99) and (100).

There are two independent interfacial parameters to be determined. The two independent relations which determine these are the energy balance relation (298) and the material balance relationships at the interface (273). We may, as in X.4.b, again circumvent the need to calculate the liquid phase mass transfer coefficient by assuming that the interfacial liquid composition is determined by the relative rates of condensation of the two species, i.e. assume that (300) holds for this case.

It is convenient to choose the interfacial temperature T_I and the liquid composition x_{1I} as the independent parameters to be determined. The best procedure for obtaining their values is to use a 2-dimensional Newton-Raphson iteration technique to search for values of T_I and x_{1I} which satisfy the relations (298) and (300).

The computational results of Krishna and Panchal (1977b) show that for rich vapour mixtures made up of species of widely different molecular sizes, diffusional interactions would have a significant influence on the design.

Krishna *et al* (1976g) have developed a design procedure for condensation of a general *n*-component mixture. They considered a sample design problem for condensation of a 6-component hydrocarbon mixture and showed that neglect of vapour phase interactions might lead to severe underdesign.

There is a great shortage of experimental data on mass transfer in multicomponent vapour (+ inert gas) liquid systems. Most of the published works deal with absorption (or condensation or evaporation) or a single species in the presence of an inert non-transferring component. A set of ternary mass transfer experiments were carried out by Toor and Sebulsky (1961) and Modine (1963) in a wetted-wall column and also in a packed column. These authors measured the simultaneous rates of transfer between a vapour–gas mixture containing acetone (1)–benzene (2)–nitrogen (3) *or* helium (3) and a binary liquid mixture of acetone and benzene. The vapour and liquid streams were in cocurrent flow for the wetted-wall column and counter-current for the packed column. Their experimental results show that diffusional interaction effects were significant in the vapour phase especially for the runs with helium as carrier gas. The theoretical model used by Toor and Sebulsky and Modine to explain their results were based on the generalized driving force approach of Toor (1957). More recently, Krishna (1979a) used the wetted-wall column experimental data of Modine (1963) to test the applicability of the Krishna and Standart (1976b) multicomponent film model and also the linearized theory of Toor and Stewart and Prober. The tests showed that both these mass transfer models which take proper account of diffusional interactions were successful in predicting the behaviour of the experimental system. On the other hand, a binary type model neglecting diffusional interactions was completely unsuccessful in this regard. The procedure for estimating multicomponent mass transfer coefficients described in section V.3 is therefore confirmed at least for systems with well-defined hydrodynamics (no surface tension or rippling phenomena).

X.5 Multicomponent Gas Absorption

The absorption of one soluble component from an inert (stagnant) carrier gas stream has been considered widely in the literature. When one soluble component is absorbed from a mixture of stagnant gases, the procedure using an effective diffusivity, defined by equation (198), is both simple and convenient. If two or more gases are being absorbed from an inert gas stream, the problem is much more complex and necessitates the use of the formalisms considered in this review. Fundamentally, the mass transfer analysis is the same as considered in X.4 for condensation of vapour mixtures. The procedure simplifies considerably for extremely lean vapour mixtures for which pseudo-binary approaches neglecting diffusional interactions will be adequate.

The calculations of Tamir and Taitel (1973) on multicomponent gas absorption give an indication of the magnitude of the interaction effects to be expected.

X.6 Ternary Mass Transfer in Liquid-Liquid Extraction

In even the simplest case of liquid extraction we must have a ternary system though most experimental extraction research work have been concerned with the case of two immiscible solvents with only one solute transferring between them. In most practical applications the solvent will have a finite miscibility in the extract phase and therefore, strictly speaking, we would have ternary mass transfer in either phase. In order to understand the effects of interaction in ternary extraction we consider a batch extraction experiment in the system 1–2–3 as depicted in Figure 1.

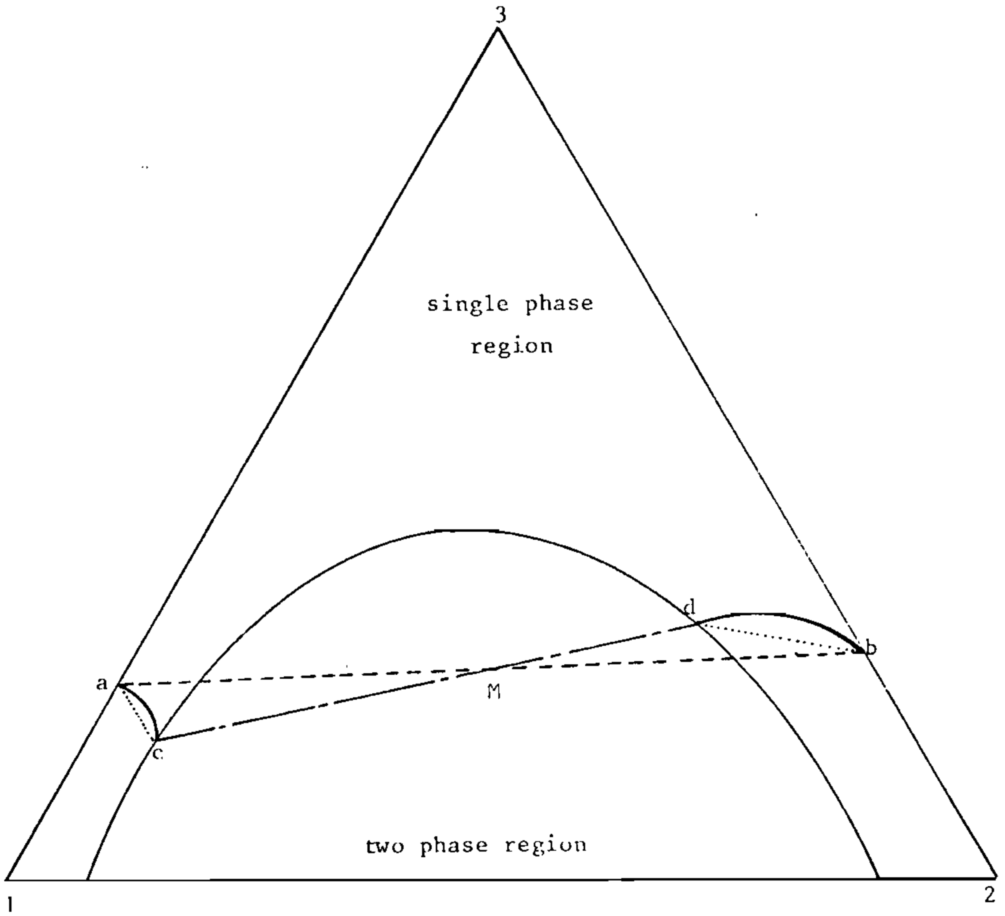

FIGURE 1. Interaction effects in ternary extraction

Let a and b represent the initial conditions of the two immiscible phases. The mixture composition is denoted by M in the figure. Let cd represent the tie line passing through the mixture composition M. During equilibration of the unsaturated phases the conditions of the two phases should change from a to c and from b to d respectively. The trajectory during this equilibration process is easily shown to be (Standart et al, 1975)

$$\frac{dx_1}{dx_2} = \frac{J_{1b}}{J_{2b}} \tag{307}$$

in either fluid phase.

If we assume a primitive mass transfer theory and use uncoupled mass transfer relations:

$$J_{ib} = k \ \Delta x_i = k \ (x_{ib} - x_{iI}), \qquad i = 1,2 \tag{308}$$

(Note that the mass transfer coefficient k must be identical for both components 1 and 2 (Toor and Arnold, 1967)), we get

$$\frac{dx_1}{dx_2} = \frac{k \Delta x_1}{k \Delta x_2} = \frac{(x_{1b} - x_{1I})}{(x_{2b} - x_{2I})} \tag{309}$$

Equation (309) shows that the tangent to the trajectory must cut binodal curve at the interfacial state (c or d). Experimental work with the system 1-acetone, 2-glycerol, 3-water (Standart et al, 1975) have shown that the tangent in one phase can miss the binodal curve entirely and the actual equilibration paths are highly curvilinear as shown in Figure 1. Such curvilinear paths can only be explained if one takes diffusional interactions into account.

Cullinan and Ram (1976) give further experimental support of the interacting mass transfer model for the system acetone–glycerol–water.

X.7 *Miscellaneous Applications*

In addition to the above examples of the applications of multicomponent mass transfer theory there are various other processes in which coupled multicomponent diffusion may play a role. These are briefly mentioned below with the appropriate entry points into the relevant literature.

By far the most dramatic effects of coupled multicomponent diffusion are likely to be found in reacting systems but unfortunately this area has not been sufficiently well explored. The theory of coupled multicomponent diffusion with reaction (homogeneous or heterogeneous) is covered by DeLancey and Chiang (1970b), DeLancey (1974), Hesse (1972–1977), Hudson (1967), Parkin (1968), Toor (1965). Experimental data are however scarce.

The calculations of Krishna (1977c) and Schneider (1978) show that the phenomena of multicomponent diffusion in porous media, where we have the combined processes of molecular and Knudsen diffusion of gaseous mixtures, may lead to important effects which have interesting consequences in determining the effectiveness and selectivities of catalytic reactions.

The necessity of considering coupling effects in multicomponent axial dispersion is emphasized by Cullinan (1973) and Sigmund (1976). Multicomponent dispersion in chemically reacting systems is considered by De Gance and Johns (1974, 1975).

The importance of coupled multicomponent diffusion in metallic systems has received a lot of attention from Kirkaldy and his co-workers and is summarized in the review of Kirkaldy (1970). Cooper (1975) gives a very good review of the importance of multicomponent diffusion in glasses.

The increasingly important area of membrane technology affords other important applications of multicomponent diffusion theories (Cussler, 1976; Krishna, 1978c). Cussler summarizes the experimental work in this area.

Some unusual examples involving coupled diffusion include:

1) diffusion of pulmonary gases in lungs (Gibbs et al, 1973)

2) accelerating the uptake of monoflurophosphate by hydroxyapatite (Breuer and Cussler, 1975)

3) solvent assisted dyeing (Butcher and Cussler, 1972)

4) drying of food liquids (Chandrasekaran and King, 1972).

NOTATION

a	interfacial area per unit volume of packed section
a	interfacial area per unit volume of dispersion on tray
A	cross-sectional area of column or tube
$\mathscr{A}_T$	element of tray area
$[A_0]$	matrix with elements given by equation (28)
(b)	column matrix of intercepts
$[B]$	matrix of inverted diffusion coefficients given by (54) and (55)
$[\mathscr{B}_0]$	matrix of inverted mass transfer coefficients given by (91) and (92)
c	molar density of fluid mixture
C_{pi}	molar heat capacity of species i
$\bar{C}_p$	mean molar heat capacity of fluid mixture
d	characteristic length of conduit or apparatus or contactor
$[D]$	matrix of practical diffusion coefficients
$\hat{D}_i$	ith eigenvalue of matrix $[D]$
$Đ_{ik}$	generalized Maxwell-Stefan diffusion coefficient
$\mathscr{D}_{ik}$	diffusion coefficient in the binary pair i–k

$\mathcal{D}_{i,\text{eff}}$	effective diffusion coefficient of species i in multicomponent mixture
E	total energy flux
$\grave{E}_{0yi}$	Murphree point vapour efficiency of species i
$[f]$	'solution' matrix for multicomponent diffusion problems
$\hat{f}_i$	solution function for pseudo-composition profiles
G_i	molar flow rate of species i
G_t	molar flow rate of fluid mixture
$[\mathcal{G}]$	matrix defined by equation (257)
h	heat transfer coefficient
h_0	heat transfer coefficient including resistances of condensate, wall and coolant
$\bar{H}_i$	partial molar enthalpy of species i in fluid mixture
ΔH_{vi}	molar heat of vaporization of species i
$\grave{HTU}_{0yi}$	pseudo-binary height of transfer unit for species i
$[I]$	indentity matrix with elements δ_{ik}
j_D, j_H	j-factors
$\mathbf{J}_i$	molar diffusion flux of species i relative to molar average velocity
$\mathbf{J}_i'$	turbulent diffusion flux
k_T	thermal conductivity of fluid mixture
k_{ik}	mass transfer coefficient of the binary pair i–k
$[k]$	matrix of multicomponent mass transfer coefficients
$\hat{k}_i$	mass transfer coefficients of pseudo-species
$\grave{k}_i$	pseudo-binary mass transfer coefficient defined by equation (202)
$[K_0]$	overall matrix of mass transfer coefficients
l	length of diffusion path in Loschmidt apparatus
$[L]$	matrix of Onsager coefficients
$[M]$	matrix of equilibrium constants
n	number of constituents in mixture
$\mathbf{N}_i$	total molar flux of species i in stationary reference frame
$\mathbf{N}_t$	total molar flux of mixture in stationary reference frame
$[NTU]$	matrix of numbers of transfer units

$N\grave{T}U_{0yi}$	pseudo-binary number of transfer units for species *i*
p_t	total system pressure
p^0_i	vapour pressure of species *i*
$[P]$	modal matrix of $[D]$
$\mathbf{q}$	conductive heat flux
q^w	heat flux through wall of condenser
R	gas constant
Re	Reynolds number
S	summation parameter in equation (67)
t	time
T	absolute temperature
$\mathbf{u}_i$	velocity of species *i* in diffusing mixture
$\mathbf{u}$	molar average velocity of mixture
V	volume of dispersion on tray
$[W]$	matrix of total mass transfer coefficients
'x'	heavy phase (e.g. liquid)
x_i	mole fraction in fluid mixture (in some cases refers specifically to liquid phase mole fraction)
y_i	mole fraction in gaseous phase
y^+_i	mole fraction in top half of Loschmidt apparatus
y^-_i	mole fraction in bottom half of Loschmidt apparatus
'y'	light phase, usually gaseous phase
$\mathbf{Y}$	thermodynamic driving force defined by equations (27)
z	distance coordinate along diffusion path
Z	distance coordinate along dispersion height, or along column height
Z	total column height

Greek Letters

α_i	dimensionless weighting factors defined in equation (195)
$[\beta]$	bootstrap solution matrix with elements given by (177) or (285)
γ_i	activity coefficient of species *i*

$[\Gamma]$	matrix of thermodynamic factors defined by equation (40)
δ	length of diffusion path, film thickness
δ_{ik}	Kronecker delta
ε	heat transfer rate factor given by equation (217)
(ξ)	column matrix with elements given by equation (90)
η	dimensionless distance along diffusion path
$[\Theta]$	matrix defined by equation (108)
λ_i	parameters defined by equation (277)
Λ_k	parameters defined by equations (105) or (283)
μ_i	molar chemical potential of species *i*
μ_x	viscosity of phase '*x*'
ξ	dimensionless distance along column or dispersion in tray
$[\Xi]$	matrix of correction factors
ρ	mass density of fluid mixture
σ	rate of production of entropy per unit volume
Υ	ratio of '11' element of square matrix to '22' element
ϕ	dimensionless mass transfer rate factor for binary system
$[\Phi]$	matrix of dimensionless rate factors for multicomponent system
ψ_i	dimensionless rate factors for pseudo-species (film theory)
Ψ_i	dimensionless rate factors for pseudo-species (penetration theory)
Ω_{12}	ratio of '12' element of square matrix to '11' element
Ω_{21}	ratio of '21' element of square matrix to '22' element

Operational Symbols

$\partial/\partial t$	spatial derivative
d/dt	material derivative following $\mathbf{u}$
∇	gradient operator
$\nabla \cdot$	divergence operator
∇^2	Laplacian or nabla operator
$\overset{n}{\Pi}$	product over *n* factors
$\lvert \quad \rvert$	determinantal operator

Δ	difference operator

Matrix Notation

$(\ )$	column matrix with $n-1$ elements
$[\ ]$	$n-1 \times n-1$ square matrix
$[\ ]^{-1}$	$n-1 \times n-1$ inverted matrix
$(\ )^T$	row matrix, $n-1$ elements
$[\ ]^T$	transposed square matrix, $n-1 \times n-1$
$\ulcorner\ \lrcorner$	diagonal matrix with $n-1$ non-zero elements
$[\ ]_s$	symmetric part of square matrix
$[\ ]_a$	anti-symmetric part of square matrix

Subscripts

av	averaged value of parameter
b	bulk phase parameter or property
c	pertaining to coolant
I	interfacial parameter or property
i,j,k	indices
n	pertaining to nth species
0	parameter at plane $z = 0$; also overall parameter
t	pertaining to total mixture
x	pertaining to phase 'x'
y	pertaining to phase 'y'
δ	parameter at plane $z = \delta$
∞	asymptotic value of parameter

Superscripts

$*$	equilibrium value
x	pertaining to phase 'x'
y	pertaining to phase 'y'

● coefficient corresponding to finite mass transfer rates

Overlines

transformed value of parameter

pseudo-binary coefficient

— averaged mixture property

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