# Diffusion and Mass Transfer in Multicomponent Mixtures of Ideal Gases

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Toor (*5, 6*) has recently presented methods of solution of the linearized equations of multicomponent mass transfer based on the generalized Fick's law relationship between fluxes and gradients. Solutions are obtained in terms of the practical diffusion coefficient matrix. Although this matrix must generally be measured directly, it may be computed from the Maxwell-Stefan equations when considering diffusion in isothermal, isobaric mixtures of ideal gases, in the absence of external fields.

This note considers the problem of obtaining this diffusion coefficient matrix or equivalent information from the Maxwell-Stefan equations. In the process Toor's method of solution of the linearized diffusion equations (*5*) and Stewart and Prober's (*4*) independent method are shown to be equivalent.

These equations may be written in the following form for a mixture of $n + 1$ components

$$-C\,\nabla y_i = \sum_{\substack{j=1\\ j\neq i}}^{n+1} \alpha_{ij}(\underline{\theta}_i y_j - \underline{\theta}_j y_i), \qquad i = 1, \ldots, n+1 \qquad (1)$$

The dependent fluxes and concentrations (and the $n + 1$th equation) may be removed by use of the restraints

$$\sum_{j=1}^{n+1} \underline{\theta}_j = 0 \qquad (2)$$

$$\sum_{j=1}^{n+1} y_j = 1 \qquad (3)$$

and after substituting into Equation (1) and converting to matrix notation

$$-(\nabla C) = \ulcorner \underline{\theta} \lrcorner \{[\beta](y) + (\alpha_{n+1})\} - \ulcorner y \lrcorner [\beta](\underline{\theta}) \qquad (4)$$

where [] represents an $n$ x $n$ matrix, $\ulcorner\ \lrcorner$ an $n$ x $n$ matrix with zeroes everywhere except on the diagonal (a diagonal matrix), and () a column vector made up of $n$ elements. The elements of the vectors and nonzero elements of the diagonal matrices are clearly either $\underline{\theta}_i$ or $y_i$, the elements of $[\beta]$ are given by

$$\beta_{ij} = \alpha_{ij} - \alpha_{i,n+1} \qquad (5)$$

with

$$\alpha_{ii} = 0,$$

and the elements of $(\alpha_{n+1})$ are $\alpha_{i,n+1}$. Let $[\beta]\ (y) = (u)$. Then, since the elements of a diagonal matrix and a vector may be interchanged, Equation (4) may be written as

$$C\,(\nabla y) = -[\ulcorner u \lrcorner + \ulcorner \alpha_{n+1} \lrcorner - \ulcorner y \lrcorner [\beta]](\underline{\theta}) \qquad (6)$$

where the diagonal elements of $\ulcorner u \lrcorner$ and $\ulcorner \alpha_{n+1} \lrcorner$ are the corresponding elements of $(u)$ and $(\alpha_{n+1})$, respectively.

Since $C$ may be taken as constant, it follows that the generalized Fick's law of interest is

$$(\underline{\theta}) = -[D]\,\nabla(C) \qquad (7)$$

with

$$[D]^{-1} = \ulcorner u \lrcorner + [\alpha_{n+1}] - \ulcorner y \lrcorner [\beta] \qquad (8)$$

$[D]$ is the multicomponent diffusivity or practical diffusion coefficient matrix.

From the earlier definitions, the off-diagonal elements of $[D]^{-1}$ are

$$y_i\,(\alpha_{i,n+1} - \alpha_{ij}) \qquad (8a)$$

and the diagonal elements are

$$\alpha_{i,n+1}\{y_i + y_{n+1}\} + \sum_{\substack{k=1\\ k\neq i}}^{n} \alpha_{ik}\, y_k \qquad (8b)$$

Stewart and Prober (*4*) give a similar equation.

Thus $[D]^{-1}$ is obtained in terms of the binary diffusion coefficients and composition. The inversion of $[D]^{-1}$ is carried out easily for a three-component system and the results are given elsewhere (*5*). The form of $[D]$ is cumbersome for more than three components but the numerical inversion may be carried out readily on a digital computer.

However, it is possible to calculate concentration profiles and mass transfer rates in multicomponent systems by the linearized theory without inverting $[D]^{-1}$, for the multicomponent mass transfer coefficient matrix, $[k]$, was shown by Toor [Equations (37) and (49) in reference 6] to be given by

$$[k] = [t]\,\ulcorner k_i \lrcorner\,[t]^{-1} \qquad (9)$$

where $[t]$ is the modal matrix of $[D]$, and the $k_i$ are appropriate binary mass transfer coefficients, which depend upon the characteristic roots of $[D]$. Since the modal matrix of $[D]^{-1}$ is the same as the modal matrix of $[D]$ and the characteristic roots of $[D]^{-1}$ are just the reciprocals of the characteristic roots of $[D]$, $[k]$ may be computed without inverting $[D]^{-1}$.

Stewart and Prober (*4*) develop their method essentially with $[D]^{-1}$ in place of the $[D]$ used by Toor and their Equation (36) is equivalent to the above Equation (9). Hence, their $k_i$ are evaluated with the characteristic roots of $[D]^{-1}$ and their modal matrix is the modal matrix of $[D]^{-1}$. In light of the discussion in the preceding paragraph, the two methods are seen to yield the same results.

Also, without inverting Equation (8) it may be noted that when $y_i \to 0$, $D_{ij} \to 0$ where $D_{ij}$ is the *ij* element of the diffusivity matrix. This does not mean, however, that species *i* is necessarily uncoupled when the concentration of *i* is small, for $\nabla C_i$ is also approaching zero as $y_i$ goes to zero. Hence, all the terms in the flux expression

$$\underline{\theta}_i = -\sum_{j=1}^{n} D_{ij}\,\nabla C_j \qquad (1')$$

vanish as $y_i \to 0$ everywhere .

If, however, components 1 to $n$, inclusive, are all dilute, then Equation (8) is a diagonal matrix which inverts to

$$[D] = \ulcorner \mathcal{D}_{i,n+1} \lrcorner \qquad (10)$$

so the dilute species are all uncoupled and show binary behavior.

The above discussion has been based on a molar reference frame. The diffusion coefficient matrix may be converted to any other desired reference frame (*5*), but once the diffusion equations are linearized [as was done in obtaining Equation (9)], there is little to be gained in converting reference frames, since the assumption of a constant *diffusivity matrix implies* small concentration changes and consequently small differences between reference velocities.

It is noted that the essential difference between the $D_{ij}$ considered here and those given by Curtiss and Hirschfelder (*2*) [also in Bird et al. (*1*)] in the mass reference frame is not due to the difference in reference frames but rather is due to the fact that the latter are defined in terms of all the gradients including the dependent one, with the diagonal elements chosen to be zero. This representation is less useful in

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# A Summary of Distributional Effects in Two-Phase Slip Models

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Slip between the phases of a two-phase stream, expressed as the ratio of average phase velocities, is an important variable affecting both operating characteristics and stability limits of such systems. Consequently, a number of models based upon different physical mechanisms have been proposed for predicting its magnitude. One explanation, first proposed by Bankoff (*1*), for at least part of the slip is that the gas phase migrates to the center of the stream where the resistance to flow and the stream velocity gradient are least. Thus, when the phase velocities are averaged over the cross section of the stream, the average magnitude of the gas velocity is greater than that of the liquid due to the distribution of the phases alone. Following Bankoff, this distributional effect has been included in several more recent models (*2, 3, 4, 6, 7*), although it is not always apparent from the analysis at which point the effect enters.

The purpose of this communication is twofold: First, to derive the distribution parameter proposed by Bankoff in a more general way, thus giving it a more general significance, and second, to show in which way this same distributional parameter or a modification of it enters the models presented in references (*2*), (*3*), (*4*), (*6*), and (*7*). However, before proceeding to our objective, it is necessary to define briefly some of the variables of a two-phase stream flowing in a tube or channel.

The cross section of a two-phase stream may be considered a probability field, at each point of which either of two mutually exclusive events may occur: either gas is present, or liquid is present. If gas is present its velocity will be $U_s$, and if liquid is present its velocity will be $U_w$. Denote the probability that gas is observed by $p$. The average magnitude of the gas velocity in this field (the cross-sectional average gas velocity) is

$$\overline{U}_s = \frac{\dfrac{1}{A}\displaystyle\int_A p\,U_s\,dA}{\dfrac{1}{A}\displaystyle\int_A p\,dA} \tag{1}$$

A similar averaging procedure gives the cross-sectional average liquid velocity. The local expectation stream velocity, $U = (1-p)\,U_w + p\,U_s$, is averaged over the flow area as follows

$$\frac{1}{A}\int_A U\,dA = \frac{1}{A}\int_A (1-p)\,U_w\,dA + \frac{1}{A}\int_A p\,U_s\,dA \tag{2}$$

Multiplying and dividing the first term on the right-hand side by $\frac{1}{A}\int_A (1-p)\,dA$ and the second term by $\frac{1}{A}\int_A p\,dA$ gives

$$\overline{U} = (1-\alpha)\,\overline{U}_w + \alpha\,\overline{U}_s \tag{3}$$

where $\alpha$ is the fraction of the cross section occupied by the gas phase (void fraction) and is related to the probability $p$ by

$$\alpha = \frac{1}{A}\int_A p\,dA \tag{4}$$

With this beginning, a general expression for Bankoff's distribution parameter can be derived.

Bankoff assumed that at each point of a two-phase stream the velocities of the phases are equal ($U_s = U_w$). He then introduced the profiles of the stream velocity and the probability as power law functions of the distance from the tube wall and integrated over the tube cross section to obtain the slip ratio relationship

$$\frac{\overline{U}_s}{\overline{U}_w} = \left[\frac{1-\alpha}{K-\alpha}\right] \tag{5}$$

where $K$ is a distributional parameter, which is a function only of the exponents of the power law profile relations.

Bankoff's assumption can be written as

$$U_s = U \tag{6}$$

and integrated over the flow area as done in Equation (1) to obtain the average gas velocity

$$\overline{U}_s = \frac{\dfrac{1}{A}\displaystyle\int_A p\,U_s\,dA}{\dfrac{1}{A}\displaystyle\int_A p\,dA} = \frac{\dfrac{1}{A}\displaystyle\int_A p\,U\,dA}{\dfrac{1}{A}\displaystyle\int_A p\,dA} \tag{7}$$

which, if we define

$$\frac{1}{K'} = \frac{\dfrac{1}{A}\displaystyle\int p\,U\,dA}{\left[\dfrac{1}{A}\displaystyle\int p\,dA\right]\left[\dfrac{1}{A}\displaystyle\int U\,dA\right]} \tag{8}$$

gives

$$\overline{U}_s = \frac{1}{K'}\,\overline{U} \tag{9}$$

Substitute Equation (3) into the right-hand side of Equation (9) and after

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mass transfer calculations than the practical diffusion coefficient form.

## ACKNOWLEDGMENT

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

## NOTATION

$C$ = total molar concentration
$C_i$ = concentration of species $i$
$\mathcal{D}_{ij}$ = binary diffusion coefficient
$D_{ij}$ = multicomponent diffusion coefficient
$[D]$ = multicomponent diffusion coefficient matrix with elements $D_{ij}$
$[k]$ = multicomponent mass transfer coefficient matrix
$k_i$ = binary mass transfer coefficients
$\lceil k_i \rfloor$ = diagonal matrix whose elements are $k_i$
$n$ = one less than the number of components
$[t]$ = modal matrix of $[D]$
$(u)$ = column vector defined by $\beta(y)$
$\lceil u \rfloor$ = diagonal matrix with elements of $(u)$
$y_i$ = mole fraction of component $i$
$(y)$ = column vector with elements $y_i$
$\lceil y \rfloor$ = diagonal matrix with elements of $y_i$
$\alpha_{ij}$ = $1/\mathcal{D}_{ij}$
$(\alpha_{n+1})$ = column vector with elements $\alpha_{i,n+1}$
$\lceil \alpha_{n+1} \rfloor$ = diagonal matrix with elements $\alpha_{i,n+1}$
$\beta_{ij}$ = defined by Equation (5)
$[\beta]$ = matrix whose elements are $\beta_{ij}$
$\underline{\theta}_i$ = molar flux of species $i$ with respect to molar average velocity, a three vector
$(\theta)$ = column vector with elements $\theta$
$\lceil \underline{\theta} \rfloor$ = diagonal matrix with elements $\underline{\theta}_i$
$\nabla$ = gradient operator

### Subscripts

$i, j, k$ = indices

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the surface, and a (horizontal) force, acting between the molecule and other adsorbed molecules in the immediate vicinity. The first of these forces depends upon the potential energy function between the surface and a single gas molecule, whereas the second can be characterized by a two-dimensional equation of state for the adsorbed layer. For an idealized homogeneous adsorbent, the characteristic potential energy between the surface and a single gaseous molecule is uniform over the surface, but for a real, heterogeneous adsorbent the potential energy is not the same for all parts of the surface since some sites are more active than others. To characterize the heterogeneity of the solid surface, the authors use a Gaussian distribution function $\Phi(U_o)$ for the characteristic adsorption potential energy $U_o$. For the equation of state of the adsorbed layer they use a two-dimensional analogue of the van der Waals equation which, through the Gibbs adsorption isotherm, may be integrated to give a fractional coverage $\theta$ at equilibrium pressure $P$ having the form $\psi(P, U_o)$. It is then shown that the experimentally obtained adsorption isotherm, up to monolayer coverage, has the general form

$$\theta = \int \Phi\ (U_o)\ \Psi\ (P, U_o)\ dU_o.$$

Perhaps the most important contribution of the book is concerned with a discussion of this integral equation. The equation has four temperature-independent molecular parameters having clear physical significance. The function $\Phi$ involves the mean characteristic potential energy of adsorption and its (Gaussian) variance, and the function $\psi$ involves the two van der Waals constants $\alpha$ and $\beta$ which are two-dimensional analogues of the familiar $a$ and $b$ in the van der Waals equation for nonideal gases. For this particular model numerical integrations are presented in tabular form at the end of the book; the calculated isotherms are matched with experimental results to yield the desired molecular parameters. This type of data reduction enables interpretation of adsorption data along rational molecular lines. According to this simple but reasonable model the variance of the adsorption energy is independent of the adsorbate but depends only on the heterogeneity of the adsorbent, and the van der Waals constants depend only on the nature of the adsorbate, being independent of the adsorbent. Only the mean characteristic potential energy of adsorption is a function of the adsorbent-adsorbate pair. Molecular parameters are presented for various gases and solids, and it is reasonable to expect that at least some of these may be correlated in terms of more readily available macroscopic properties.

In addition to a detailed analysis of the heterogeneous solid-mobile gas model, the authors devote a chapter to a lucid discussion of the various heats of adsorption and their interrelation, and another chapter to a generous treatment of intermolecular potentials between solids and adsorbed gases. The latter, unfortunately, does not include any mention of the effect of nonadditivity which, as Sinanoglu and Pitzer have shown, is by no means negligible.

Dr. Ross, Professor of Colloid Science at Rensselaer Polytechnic Institute, and his former student and associate, Dr. Olivier, have performed a valuable service to the chemical profession in summarizing the present state of monolayer physical adsorption, a subject to which Professor Ross and his co-workers have contributed much original material. As pointed out in the foreword by Professor de Boer, the complex subject of the physical adsorption of gases on solids, which has for so long been known only empirically, is now at last beginning to stand on a sound theoretical foundation, one on which future research workers may build with confidence. This well-written monograph will serve admirably to introduce interested chemical engineers to one of the fascinating frontiers of current research in molecular thermodynamics.

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**Process Systems Analysis and Control,** Donald R. Coughanowr and Lowell B. Koppel, McGraw-Hill Book Company, Inc., New York (1965), 491 pages, $15.50.

Although it has become apparent in recent years that one of the major areas of application of control systems is the chemical and petroleum industries, there has been a decided lack of textbooks written for the chemical engineer and the chemist that deal with this type of analysis. The current book is therefore welcome as an attempt to familiarize the chemical engineer with available process control techniques from both an analytical and a simulation point of view.

The first half of the book is devoted to linear-systems analysis of such topics as open- and closed-loop systems, root

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