1 = heat transfer
2 = mass transfer
$m$ = maximum value
$n$ = minimum value
$s$ = steady state

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# Multicomponent Mass Transfer in Turbulent Flow

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The purpose of this note is to give a method for predicting multicomponent eddy diffusivities and to correct the recent analysis of von Behren et al. (1972). The new results are simpler and more accurate.

### PREDICTION OF EDDY DIFFUSIVITIES

The diffusion equations of a nonreacting fluid in laminar or turbulent flow can be written in an uncoupled form (Stewart and Prober, 1964; Toor, 1964):

$$\frac{\partial \check{x}_i}{\partial t} + (\nabla \bullet \mathbf{v}^{\star} \check{x}_i) = \check{D}_i \nabla^2 \check{x}_i \quad i = 1, \ldots n - 1 \qquad (1)$$

Here the $\check{D}_i$ are the inverted eigenvalues of Stewart and Prober's matrix $[A]$, and the $\check{x}_i$ are the corresponding transformed compositions. The $\bar{x}_i$ of that paper are written as $\check{x}_i$ here, to distinguish them from time-smoothed quantities.

Time-smoothing Equation (1), we get

$$\frac{\partial \bar{\check{x}}_i}{\partial t} + (\nabla \bullet \bar{\mathbf{v}}^{\star} \bar{\check{x}}_i) = \check{D}_i \nabla^2 \bar{\check{x}}_i - (\nabla \bullet \overline{\mathbf{v}^{\star\prime} \check{x}_i'}) \qquad i = 1, \ldots n - 1 \qquad (2)$$

If the correlation term is rewritten with an eddy diffusivity tensor $\check{\mathbf{D}}_i^{(t)}$, Equation (2) becomes

$$\frac{\partial \bar{\check{x}}_i}{\partial t} + (\nabla \bullet \bar{\mathbf{v}}^{\star} \check{x}_i) = \check{D}_i \nabla^2 \bar{\check{x}}_i + (\underline{\nabla} \bullet \check{\mathbf{D}}_i^{(t)} \bullet \nabla \bar{\check{x}}_i) \qquad i = 1, \ldots n - 1 \qquad (3)$$

Equations (1), (2), and (3) are analogous to the following equations of binary systems:

$$\frac{\partial x_A}{\partial t} + (\nabla \bullet \mathbf{v}^{\star} x_A) = \mathcal{D}_{AB} \nabla^2 x_A \qquad (4)$$

$$\frac{\partial \bar{x}_A}{\partial t} + (\nabla \bullet \bar{\mathbf{v}}^{\star} \bar{x}_A) = \mathcal{D}_{AB} \nabla^2 \bar{x}_A - (\nabla \bullet \overline{\mathbf{v}^{\star\prime} x'_A}) \qquad (5)$$

$$\frac{\partial \bar{x}_A}{\partial t} + (\nabla \bullet \bar{\mathbf{v}}^{\star} \bar{x}_A) = \mathcal{D}_{AB} \nabla^2 \bar{x}_A + (\nabla \bullet \mathbf{D}_{AB}^{(t)} \bullet \nabla \bar{x}_A) \qquad (6)$$

Thus, any solution of Equation (4), (5), or (6) provides a solution of Equation (1), (2), or (3) in the same flow field, satisfying equivalent boundary conditions. The corresponding, numerically equal quantities are

$$\left.\begin{array}{l} \mathcal{D}_{AB} \rightarrow \check{D}_i \\ x_A \rightarrow \check{x}_i \\ \overline{x}_A \rightarrow \overline{\check{x}}_i \\ \overline{\mathbf{v}^{\star\prime} x'_A} \rightarrow \overline{\mathbf{v}^{\star\prime} \check{x}_i'} \\ \mathbf{D}_{AB}^{(t)} \rightarrow \check{\mathbf{D}}_i^{(t)} \end{array}\right\} \qquad (7)$$

Thus, to evaluate $\check{\mathbf{D}}_i^{(t)}$, one uses the eddy diffusivity $\mathbf{D}_{AB}^{(t)}$ of a corresponding binary system. This result is implicit in the first two correspondences of Equation (7), which were proved by Stewart and Prober (1964).

Equations (6) are equivalent to the following differential equation for the mole fractions:

$$\frac{\partial}{\partial t}[\overline{x}] + (\nabla \bullet \mathbf{v}^{\star}[\overline{x}]) = [D]\nabla^2[\overline{x}] + (\nabla \bullet [\mathbf{D}^{(t)}] \bullet \nabla [\overline{x}]) \qquad (9)$$

with

$$[D] = [P]\,[\check{D}]\,[P]^{-1} \qquad (10)$$

and

$$[\mathbf{D}^{(t)}] = [P]\,[\check{\mathbf{D}}^{(t)}]\,[P]^{-1} \qquad (11)$$

The matrix $[P]$ is found from $[A]$ as in Stewart and Prober (1964). Equation (9) is interesting, but not essential; for actual calculations it is usually simpler to use Equations (3) and (7), with the $\check{D}_i$ obtained from $[A]$.

Von Behren et al. start with an equation similar to (9), except for the final term. In place of $[\mathbf{D}^{(t)}]$, they use a matrix $[\epsilon]$ with all elements assumed to be equal. This assumption is clearly in error since it predicts equality of the turbulent fluxes for all species but the last.

If the eddy diffusivities are independent of the molecular ones, then the $\check{\mathbf{D}}^{(t)}$ of Equation (3) are independent of *i*. Then Equation (11) gives

$$[\mathbf{D}^{(t)}] = [\check{\mathbf{D}}^{(t)}] = [I]\mathbf{D}_1^{(t)} \qquad (12)$$

To this approximation, the turbulent diffusion terms are uncoupled in Equation (9) as well as Equation (3). Hence the matrix $[\epsilon]$ of von Behren et al. should have been written with zeroes as the off-diagonal elements.

It should be emphasized that generality is lost, not gained, by time-smoothing the equations of change. Equation (3) is useful only as a means of estimating smoothed solutions, whereas Equation (1) describes the fluctuations. Equation (1) has proved quite tractable for making predictions from experiments (Stewart and Prober, 1964; Toor, 1964).

## PREDICTION OF MASS TRANSFER RATES

The mass transfer predictions of von Behren et al. (1972) are for developed turbulent flow in a pipe, with a uniform upstream composition $[x_1]$ and a step change in interfacial state from $[x_1]$ to $[x_0]$. The local fluxes can be found from Equation (36) of Stewart and Prober (1964),

$$[N_0 - x_0 \sum_{j=1}^{n} N_{j0}] = [P]\,[\check{k}^{\bullet}_x]\,[P]^{-1}\,[x_0 - x_1] \qquad (13)$$

and the insolubility condition

$$N_{n0} = 0 \qquad (14)$$

of the given problem. Here $[\check{k}^{\bullet}_x]$ is a diagonal matrix of mass transfer coefficients $\check{k}^{\bullet}_{xi}$ based on the driving forces $(\check{x}_{i0} - \check{x}_{i1})$. For simplicity we treat all variables in (13) as time-smoothed.

The transfer coefficients $\check{k}^{\bullet}_{xi}$ can be predicted from results for turbulent heat transfer with a step change in wall temperature. The series solution of Sleicher and Tribus (1957) can be written

$$h = \frac{4k_a}{D} \sum_{m=0}^{\infty} A_m \exp\left(-\lambda_m^2 \frac{2z}{D\,Re\,Pr}\right) \qquad (15)$$

with $h = q_0/(T_0 - T_1)$. The $A_m$ and $\lambda_m^2$ are functions of *Re* and *Pr*; results for $m \leqq 2$ are plotted in their paper. Insertion of analogous notations for mass transfer gives

$$k_{xi} \overset{\wedge}{=} \frac{4c_a\check{D}_i}{D} \sum_{n=0}^{\infty} A_{mi} \exp\left(-\lambda_{mi}^2 \frac{2z}{D\,Re\,Sc_i}\right) \qquad i = 1, \ldots n-1 \qquad (16)$$

Here the $A_{mi}$ and $\lambda_{mi}^2$ are evaluated like $A_m$ and $\lambda_m^2$, but at $Sc_i = (\mu_a/\rho_a\check{D}_i)$ instead of *Pr*.

Use of the film theory to correct for the normal velocity at the interface gives (Stewart and Prober, 1964):

$$\check{k}^{\bullet}_{xi} = \check{k}_{xi} \frac{\check{\phi}_{xi}}{(e^{\check{\phi}_{xi}} - 1)} \qquad i = 1, \ldots n-1 \qquad (17)$$

$$\check{\phi}_{xi} = \sum_{j=1}^{n} N_{j0}/k_{xi} \qquad i = 1, \ldots n-1 \qquad (18)$$

With $[\check{k}^{\bullet}_x]$ constructed from these calculations, the fluxes $N_{j0}$ can be found by simultaneous solution of Equations (13) and (14). The solution is iterative since the $\check{k}^{\bullet}_{xi}$ depend on the unknown fluxes $N_{j0}$.

Iteration can be avoided by linearizing Equation (17) as follows:

$$\check{k}^{\bullet}_{xi} = \check{k}_{xi} + \frac{1}{2} \sum_{j=1}^{n} N_{j0} + O\left(\sum_{j=1}^{n} N_{j0}\right)^2 \qquad i = 1, \ldots n-1 \qquad (19)$$

With this approximation, valid for moderate net transfer rates, Equation (13) becomes

$$\left[N_0 - \frac{1}{2}(x_0 + x_1) \sum_{j=1}^{n} N_{j0}\right] \doteq [P]\,[\check{k}^{\bullet}_x]\,[P]^{-1}\,[x_0 - x_1] \qquad (20)$$

and the solution for the fluxes $N_{j0}$ is direct.

The relative evaporation rates $N_{j0}/N_{10}$ are functions of $z$ unless all the $Sc_i$ are equal. Hence, the constant-evaporating condition $[N_0] = (\text{const.})\,[x_0]$ generally will not hold for the whole surface even if $[x_0]$ is an azeotropic composition. This presents a difficulty in analyzing the measurements of von Behren et al. but probably a minor one in comparison with the serious nonuniformity of their wall temperature, and hence of $[x_0]$.

A more accurate calculation could be made by integrating Equations (3) or (9) with a corrected velocity field $\overline{\mathbf{v}}^\star$. This is difficult because $\overline{\mathbf{v}}^\star$ depends on all the composition gradients, through Equation (14):

$$\overline{v_0}^\star \, \overline{x}_{n0} = - \sum_{i=1}^{n-1} \sum_{j=1}^{n-1} D_{ij} \frac{\partial \overline{x}_j}{\partial y} \bigg|_{y=0} \qquad (21)$$

or, in the variables of Equation (3),

$$\overline{v_0}^\star \left( 1 - \sum_{j=1}^{n-1} \sum_{i=1}^{n-1} P_{ij} \overline{\check{x}}_{j0} \right)$$

$$= - \sum_{j=1}^{n-1} \sum_{i=1}^{n-1} P_{ij} \check{D}_j \frac{\partial \overline{\check{x}}_j}{\partial y} \bigg|_{y=0} \qquad (22)$$

This boundary condition makes it necessary to solve all the differential equations at once, despite the uncoupled form of Equation (3). Equations (16) to (20) handle the coupling more easily, by starting from the simple case of vanishing net mass transfer rate. Other types of constraints on the $N_{j0}$ and $x_{i0}$ can be handled analogously, for constant $[x_0]$, by solving them simultaneously with Equation (13).

Von Behren et al. treat the boundary conditions differently. In their Equation (11), they assume that each eigenfunction $\check{x}_i$ behaves as $x_A$ would in binary diffusion through stagnant $B$. This assumption is contradictory, since it treats each eigenfunction both as stagnant and transferable. As a result, their Equation (11) gives $n - 1$ different solutions for $\overline{\mathbf{v}}^\star$, none of which satisfy Equation (14).

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## NOTATION

$[A]$ = matrix of order $n - 1$, $m^{-2}s$. For ideal gaseous systems, the Stefan-Maxwell equations give

$$A_{ij} = (x_i/\mathcal{D}_{in})_a - (x_i/\mathcal{D}_{ij})_a + \delta_{ij} \sum_{k=1}^{n} (x_k/\mathcal{D}_{ik})_a$$

$c$ = molar density, k-moles $m^{-3}$
$D$ = pipe diameter, m
$[D]$ = diffusivity matrix based on $[x]$, $m^2 s^{-1}$
$\check{D}_i$ = diffusivities based on $[\check{x}]$, found as inverted eigenvalues of $[A]$, $m^2 s^{-1}$
$[\check{D}]$ = diffusivity matrix based on $[\check{x}]$, $[\text{diag}\,(\check{D}_1, \ldots \check{D}_{n-1})]$
$[\mathbf{D}^{(t)}]$ = turbulent diffusivity matrix based on $[x]$, $m^2 s^{-1}$
$\check{\mathbf{D}}_i^{(t)}$ = turbulent diffusivity tensors based on $[\check{x}]$, $m^2 s^{-1}$
$[\check{\mathbf{D}}^{(t)}]$ = turbulent diffusivity matrix based on $[\check{x}]$, $[\text{diag}\,(\check{\mathbf{D}}_1^{(t)}, \ldots \check{\mathbf{D}}_{n-1}^{(t)})]$
$\mathcal{D}_{AB}$ = ordinary diffusivity of pair $A$, $B$ at given $c$ and $T$, $m^2 s^{-1}$
$\underset{\sim}{\mathcal{D}}_{AB}^{(t)}$ = turbulent diffusivity tensor of binary system $A - B$, $m^2 s^{-1}$
$h$ = heat transfer coefficient, $Wm^{-2} K^{-1}$
$[I]$ = unit matrix of order $n - 1$
$k$ = thermal conductivity, $Wm^{-1} K^{-1}$
$\check{k}_{xi}$ = mass transfer coefficient based on $\check{x}_i$, at $\check{\phi}_{xi} = 0$, k-mole $m^{-2} s^{-1}$
$[\check{k}_x]$ = matrix, $[\text{diag}\,(\check{k}_{x1}, \ldots \check{k}_{xn-1})]$
$\check{k}^\bullet_{xi}$ = mass transfer coefficient based on $\check{x}_i$ and corrected to $\check{\phi}_{xi}$, k-mole $m^{-2} s^{-1}$
$[\check{k}^\bullet_x]$ = matrix, $[\text{diag}\,(\check{k}^\bullet_{x1}, \ldots \check{k}^\bullet_{xn-1})]$
$N_{j0}$ = interfacial molar flux of species $j$ into stream, k-mole $m^{-2} s^{-1}$
$[N_0]$ = column vector with elements $N_{10}, \ldots N_{n-1,0}$
$[P]$ = matrix of right-hand eigenvectors of $[A]$, dimensionless
$q_0$ = interfacial conductive heat flux into stream, $Wm^{-2}$
$Re$ = Reynolds number, $DG/\mu_a$, dimensionless
$Pr$ = Prandtl number, $(\hat{C}_p\mu/k)_a$, dimensionless
$Sc_i$ = Schmidt number based on $\check{x}_i$, $\mu_a/\rho_a\check{D}_i$, dimensionless
$T$ = temperature, K
$\mathbf{v}^\star$ = molar average velocity vector, m $s^{-1}$
$v_0^\star$ = $y$-component of $\mathbf{v}^\star$ at $y = 0_+$, $\sum_{j=1}^{n} N_{j0}/c_a$, m $s^{-1}$
$x_i$ = mole fraction of species $i$
$[x]$ = column vector with elements $x_1, \ldots x_{n-1}$
$\check{x}_i$ = transformed composition, $i^{\text{th}}$ element of $[\check{x}]$
$[\check{x}]$ = $[P]^{-1}[x]$
$y$ = normal distance from interface into stream, m
$z$ = downstream distance from start of heat or mass transfer region, m

### Greek Letters

$\mu$ = viscosity, k $m^{-1} s^{-1}$
$\rho$ = density, k $m^{-3}$
$\check{\phi}_{xi}$ = dimensionless net molar flux defined in (18)

### Subscripts

$A, B$ = species in binary mixture
$a$ = evaluated at an average state, 0.5 $(T_0 + T_1)$ or 0.5 $[x_0 + x_1]$
$i, j$ = species, and also eigenfunctions, in multicomponent mixtures
0 = at $y = 0_+$
1 = in entering stream at $z = 0$

### Superscripts and Overlines

$\star$ = molar average
$(t)$ = turbulent
$\bullet$ = corrected for net molar flux
— = time-smoothed function
$'$ = fluctuation from time-smoothed function
$\vee$ = based on the transformed compositions $\check{x}_i$

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