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# A NOTE ON MULTICOMPONENT MASS TRANSFER IN TURBULENT FLOW

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ABSTRACT
We consider mass transfer in turbulent flow of multicomponent mixtures, taking into account the molecular diffusional coupling between the constituent species. For steady state transport across an effective 'film', we develop a simple analytic procedure for calculating the matrix of multicomponent mass transfer coefficients.

## Analysis

The continuity relations for diffusion in an n-component mixture in molar units take the form [1]

$$\frac{\partial c_i}{\partial t} + \underset{\sim}{\nabla} \cdot c_i \, \underset{\sim}{u}_i = \frac{\partial c_i}{\partial t} + \underset{\sim}{\nabla} \cdot \underset{\sim}{N}_i = 0, \qquad i = 1,2,..n \tag{1}$$

where

$$\underset{\sim}{N}_i = c_i \, \underset{\sim}{u}_i = c_i \, (\underset{\sim}{u}_i - \underset{\sim}{u}) + c_i \, \underset{\sim}{u} = \underset{\sim}{J}_i + x_i \, \underset{\sim}{N}_t \tag{2}$$

is the total molar flux of species i; $J_i$ is the molar diffusion flux of i with respect to the molar average reference velocity $\underset{\sim}{u}$; $\underset{\sim}{N}_t = c \, \underset{\sim}{u}$ is the total mixture molar flux; c is the total mixture molar concentration.

Summing equations (1) over the n species we have for the total mixture

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$$\frac{\partial c}{\partial t} + \nabla \cdot c\, u = \frac{\partial c}{\partial t} + \nabla \cdot N_t = 0 \qquad (3)$$

A combination of equations (1) - (3) gives differential relations in terms of the constituent mole fractions $x_i$

$$c \left( \frac{\partial x_i}{\partial t} + u \cdot \nabla x_i \right) = - \nabla \cdot J_i, \qquad i = 1,2,..n-1 \qquad (4)$$

where we write only n-1 independent relations.

For multicomponent mixtures we must take account of the diffusional coupling and write the molar diffusion fluxes as [2,3,4]

$$J_i = - c \sum_{j=1}^{n-1} D_{ij} \nabla x_j, \qquad i = 1,2,..n-1 \qquad (5)$$

where $[D]$ represents an $\underline{n-1}\times\underline{n-1}$ square matrix of molecular diffusion coefficients.

Equations (4) and (5) represent a set of n-1 coupled partial differential equations. By assuming that c and $D_{ij}$ are constant along the diffusion path, these equations may be uncoupled by use of the similarity transformation as discussed by Toor [2] and Stewart and Prober [3]. We address ourselves to the problem of diffusion under turbulent flow conditions. In his analysis of this problem, Stewart [4] first diagonalizes (4) and (5) and obtains

$$\frac{\partial \hat{x}_i}{\partial t} + \nabla \cdot (\hat{x}_i\, u) = \nabla \cdot ( \hat{D}_i \nabla \hat{x}_i), \qquad i = 1,2,..n-1 \qquad (6)$$

where the $\hat{D}_i$ represent the eigenvalues of the matrix $[D]$:

$$[P]^{-1} [D] [P] = \ulcorner \hat{D} \lrcorner \qquad (7)$$

and the pseudo compositions $\hat{x}_i$ are given by

$$(\hat{x}) = [P]^{-1} (x) \qquad (8)$$

On time averaging the instantaneous relations (6) we have

$$\begin{aligned} \frac{\partial \overline{\hat{x}_i}}{\partial t} + \nabla \cdot ( \overline{\hat{x}_i}\ \overline{u}) &= \nabla \cdot ( \hat{D}_i \nabla \overline{\hat{x}_i} - \overline{\hat{x}_i' u'} ) \\ &= \nabla \cdot ( \hat{D}_i \nabla \overline{\hat{x}_i} + \sum_{j=1}^{n-1} D^t_{ij} \nabla \overline{\hat{x}_j}) \end{aligned} \qquad (9)$$

The turbulent diffusion flux can be written as

$$\underset{\sim}{J}_i^t \equiv - c \sum_{j=1}^{n-1} D_{ij}^t \underset{\sim}{\nabla} x_j \equiv c \overline{x_i' \, \underset{\sim}{u}'}, \qquad i = 1,2..n-1 \quad (10)$$

where $D_{ij}^t$ are elements of the turbulent diffusivity matrix. If we assume that the turbulent diffusivities are independent of the molecular diffusivities then the turbulent diffusivity matrix must simplify as [4,5]:

$$[D^t] = D^t \ulcorner I \lrcorner \; ; \qquad D_{ij}^t = D^t \delta_{ij}, \qquad i,j = 1,2,..n-1 \quad (11)$$

and we must have

$$\hat{D}_{ij}^t = D^t \delta_{ij}, \qquad i,j = 1,2,..n-1 \quad (12)$$

so

$$\frac{\partial \overline{\hat{x}_i}}{\partial t} + \underset{\sim}{\nabla} \cdot ( \overline{\hat{x}_i} \, \overline{\underset{\sim}{u}} ) = \underset{\sim}{\nabla} \cdot (( \hat{D}_i + D^t) \underset{\sim}{\nabla} \overline{\hat{x}_i}) \quad (13)$$

Note that $D^t$ (and indeed $D_{ij}^t$) can vary with position and time; they only must not be functions of composition, else we cannot apply the inverse transformation.

Alternatively we can time average equations (4)-(5) first when we get on dividing by c

$$\frac{\partial \overline{x}_i}{\partial t} + \underset{\sim}{\nabla} \cdot ( \overline{x}_i \, \overline{\underset{\sim}{u}} ) = \underset{\sim}{\nabla} \cdot \{ \sum_{j=1}^{n-1} (D_{ij} + D_{ij}^t) \underset{\sim}{\nabla} \overline{x}_j \} \quad (14)$$

Now to diagonalize equation (14) is more complicated for we must find the eigenvalues of $D_{ij} + D_{ij}^t$. If equation (11) applies, we may however just find the eigenvalues and modal matrix [P] for [D], when the diagonal form of equation (14) becomes identical to equation (13). Thus Stewart's [4] approach is mathematically more elegant but conceptually requires us to consider justifying equation (10) for turbulent diffusion flux in diagonalized form, i.e. in terms of pseudovariables.

The important point is that whichever method is used, we come to equation (13) as one which we must solve in order to obtain the composition profiles and fluxes. We develop below the integrations of equation (13) for the simple case of one-dimensional steady state diffusion.

Thus we have in n-1 dimensional matrix notation (we omit the overbars for simplicity)

$$u \frac{d(\hat{x})}{dz} = \frac{d}{dz} \left\{ \left[ \ulcorner \hat{D} \lrcorner + D^t \ulcorner I \lrcorner \right] \frac{d(\hat{x})}{dz} \right\} \qquad (15)$$

with a position dependent $D^t$

$$D^t = D^t (z) \qquad (16)$$

The first integral of (15) is

$$c\, u\, (\hat{x}) = (\hat{x})\, N_t = (\hat{x})_0\, N_t + c \left[ \ulcorner \hat{D} \lrcorner + D^t \ulcorner I \lrcorner \right] \frac{d(\hat{x})}{dz}$$

$$- c \left[ \ulcorner \hat{D} \lrcorner + D_0^t \ulcorner I \lrcorner \right] \left. \frac{d(x)}{dz} \right)_0 \qquad (17)$$

where at the rigid wall or interface, $z = 0$, we may take $D_0^t = 0$. The equation (17) says no more than

$$N_i = N_{i0};\ \hat{N}_i = \hat{N}_{i0}, \qquad i = 1,2,..n-1 \qquad (18)$$

an uncoupled linear first order differential equation better written as

$$- c \left( \hat{D}_i + D^t (z) \right) \frac{d\hat{x}_i}{dz} + \hat{x}_i N_t = \hat{N}_{i0} \qquad (19)$$

with integrating factor

$$\exp \left( - \frac{N_t}{c} \int_0^z \frac{dz}{\hat{D}_i + D^t(z)} \right) \equiv \exp\left( - F_i(z) \right) \qquad (20)$$

so

$$\hat{x}_{iz} = e^{F_i(z)} \left( \hat{x}_{i0} + \int_0^z \frac{\hat{N}_{i0}\, e^{-F_i(z)}\, dz}{c\, (\hat{D}_i + D^t(z))} \right)$$

$$= e^{F_i(z)} \left( \hat{x}_{i0} - \frac{\hat{N}_{i0}}{N_t} \left( e^{-F_i(z)} - 1 \right) \right) \qquad (21)$$

Writing

$$\hat{\phi}_{i0} \equiv \hat{N}_{i0} / N_t \qquad (22)$$

we have

$$\hat{x}_{iz} + \hat{\phi}_{i0} = (\hat{x}_{i0} + \hat{\phi}_{i0})\, e^{F_i(z)} \tag{23}$$

and at the plane $z = \delta$, where $\delta$ may be viewed as the film thickness for mass transfer, we have

$$\hat{x}_{i\delta} + \hat{\phi}_{i0} = (\hat{x}_{i0} + \hat{\phi}_{i0})\, e^{F_i(\delta)} \tag{24}$$

and therefore we have

$$\frac{\hat{x}_{iz} - \hat{x}_{i0}}{\hat{x}_{i\delta} - \hat{x}_{i0}} = \frac{e^{F_i(z)} - 1}{e^{F_i(\delta)} - 1} \tag{25}$$

Now at the wall

$$\hat{J}_{i0} \equiv - c\, \hat{D}_i \left.\frac{d\hat{x}_i}{dz}\right|_0 = \frac{N_t\, (\hat{x}_{i0} - \hat{x}_{i\delta})}{e^{F_i(\delta)} - 1} =$$

$$= \frac{\hat{k}_i\, \hat{\psi}_i\, (\hat{x}_{i0} - \hat{x}_{i\delta})}{e^{F_i(\delta)} - 1} \tag{26}$$

where

$$\hat{\psi}_i \equiv N_t / \hat{k}_i \equiv N_t / (c\, \hat{D}_i / \delta) \tag{27}$$

or

$$\hat{J}_{i0} \equiv \hat{k}^{\bullet}_{i0}\, (\hat{x}_{i0} - \hat{x}_{i\delta}) \tag{28}$$

with

$$\hat{k}^{\bullet}_{i0} = \frac{\hat{k}_i\, \hat{\psi}_i}{e^{F_i(\delta)} - 1} = \hat{k}_i\, \frac{\hat{\psi}_i}{e^{\hat{\psi}_i} - 1}\, \frac{e^{\hat{\psi}_i} - 1}{e^{F_i(\delta)} - 1} \tag{29}$$

with a high flux correction factor $\hat{\psi}_i/(\exp \hat{\psi}_i - 1)$ and a turbulence intensity factor $(\exp \hat{\psi}_i - 1)/(\exp F_i(\delta) - 1)$.

The $\hat{k}^{\bullet}_{i0}$ are the high flux mass transfer coefficients for the pseudo-species and these coefficients can be estimated from the physical, thermodynamic, transport and turbulence parameters as given by equation (29). We first discuss the evaluation of the $F_i(\delta)$ and later discuss the transformation of equation (29) to obtain the transfer coefficients for the actual species.

The turbulent diffusivity is best expressed in terms of the dimensionless distance from the wall $y^+$ defined as

$$y^+ \equiv u^* z / \nu \tag{30}$$

Let us write the pseudo diffusion fluxes as

$$\hat{J}_i \equiv -c\,(\hat{D}_i + D^t)\frac{d\hat{x}_i}{dz}$$

$$= -c\,u^*\,(\hat{D}_i/\nu + D^t/\nu)\frac{d\hat{x}_i}{dy^+} \tag{31}$$

and so defining the Schmidt numbers

$$\hat{Sc}_i \equiv \nu/\hat{D}_i \;;\quad Sc_{ij} \equiv \nu/D_{ij} \tag{32}$$

we have

$$\frac{\hat{J}_i}{N_t} = -\frac{c\,u^*}{N_t}\left(1/\hat{Sc}_i + \frac{D^t(y^+)}{\nu}\right)\frac{d\hat{x}_i}{dy^+} \tag{33}$$

Thus

$$F_i(z) = f_i(y^+) \equiv \frac{N_t}{cu^*}\int_0^{y^+}\frac{dy^+}{\dfrac{1}{\hat{Sc}_i} + \dfrac{D^t(y^+)}{\nu}} \tag{34}$$

Any reasonable turbulence model can now be substituted for $D^t(y^+)/\nu$ and the integral in equation (34) evaluated, and the fluxes of the pseudo-species calculated from equation (33).

It now remains to obtain an expression for the matrix of multicomponent mass transfer coefficients $[k^{\bullet}]$ defined usually as [2-4]

$$(J) = [k^{\bullet}] (x_0 - x_\delta) \tag{35}$$

where the diffusion fluxes $J_i$ are related to the pseudo diffusion fluxes by the similarity transformation

$$(J) = [P] (\hat{J}) \tag{36}$$

Thus if we premultiply equation (28), in its matrix form, by [P] we have after using equation (8)

$$(J) = [P] \ulcorner \hat{k}^{\bullet} \lrcorner [P]^{-1} (x_0 - x_\delta) \tag{37}$$

A combination of equations (35) and (37) leads us to the final predictive relation for the matrix of multicomponent mass transfer coefficients

$$[k^{\bullet}] = [P] \ulcorner \hat{k}^{\bullet} \lrcorner [P]^{-1} \tag{38}$$

## Conclusions

We have analysed the problem of n-component diffusion in turbulent flow under steady state conditions. In the analysis we have allowed for the possibility of molecular diffusional coupling between the species. By assuming an arbitrary model for the turbulent diffusivity, equation (16), we have obtained an analytic expression for the composition profiles across a plane of thickness $\delta$. The differentiation of the composition profiles gave the mass transfer coefficients in terms of the physical and turbulence parameters. One of the novel results of this study has been the expression (29), with equation (38), in which we have separated the effects of bulk flow (finite mass transfer [1]) and turbulence.

## Nomenclature

| | |
|---|---|
| $c$ | total molar density of the mixture |
| $c_i$ | molar density of species i in n-component mixture |
| $D_{ij}$ | elements of the matrix of Fickian diffusion coefficients, defined by equations (5) |
| $\hat{D}_i$ | eigenvalues of the matrix [D]; also diffusion coefficients of the pseudo species i |

| | |
|---|---|
| $D^t$ | turbulent eddy diffusivity |
| $D^t_{ij}$ | elements of the matrix of turbulent diffusivities |
| $F_i(z)$ | function defined by equation (20) |
| $f_i(y^+)$ | function defined by equation (34) |
| $[I]$ | identity matrix with elements $\delta_{ik}$ |
| $J_i$ | diffusion fluxes of species i |
| $\hat{J}_i$ | diffusion fluxes of the pseudo species i |
| $J^t_i$ | turbulent diffusion flux |
| $\hat{k}_i$ | pseudo-coefficients defined by equation (27) |
| $\hat{k}^\bullet_i$ | pseudo-high flux mass transfer coefficients defined by equation (28) |
| $[k^\bullet]$ | matrix of multicomponent mass transfer coefficients |
| n | number of components in mixture |
| $\underset{\sim}{N}_i$ | molar flux of species i relative to a stationary frame of reference |
| $\underset{\sim}{N}_t$ | molar flux of total mixture relative to a stationary frame of reference |
| $\hat{N}_{i0}$ | molar flux of pseudo species i at the plane z=0 |
| $[P]$ | modal matrix of $[D]$ |
| Sc | Schmidt number |
| t | time |
| $\underset{\sim}{u}_i$ | velocity of species i |
| $\underset{\sim}{u}$ | molar average velocity of mixture |
| u* | friction velocity |
| $x_i$ | mole fraction of species i in mixture |
| $\hat{x}_i$ | mole fraction of the pseudo-species |
| $\overline{x}_i$ | time averaged compositions |
| $\overline{\hat{x}}_i$ | time averaged pseudo-compositions |
| $y^+$ | dimensionless distance defined by equation (30) |
| z | distance parameter |

Greek Letters

| | |
|---|---|
| $\delta$ | length of diffusion path |
| $\delta_{ik}$ | Kronecker delta |
| $\nu$ | kinematic viscosity |
| $\hat{\phi}_i$ | factor defined by equation (22) |
| $\hat{\psi}_i$ | factor defined by equation (27) |

Operational Symbols

| | |
|---|---|
| $\partial/\partial t$ | spatial derivative |
| $\underset{\sim}{\nabla}$ | gradient operator |
| $\underset{\sim}{\nabla}\cdot$ | divergence operator |
| d/dz | scalar gradient operator |

Matrix Notation

| | |
|---|---|
| ( ) | column matrix with $\underline{n-1}$ elements |
| [ ] | square matrix $\underline{n-1}\times\underline{n-1}$ |
| $[\ ]^{-1}$ | inverted square matrix |
| ⌜ ⌟ | diagonal matrix |

Subscripts

| | |
|---|---|
| i,j | indices usually referring to constituent species |
| t | pertaining to total mixture |
| z | at plane z=z |
| 0 | at plane z=0 |
| $\delta$ | at plane $z=\delta$ |

Superscripts

| | |
|---|---|
| t | turbulent parameter |
| • | coefficient under finite mass transfer conditions |
| + | non-dimensional turbulence parameter |
| * | friction velocity |
| ^ | pseudo species |
| — | overbar denotes time averaged quantities |

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