rates, but the spatial growth becomes weaker as the flow rate vanishes. In contrast, the time steady spacially growing instability leading to dry patches appears only below a critical Reynolds number and becomes stronger as the Reynolds number decreases.

NOTATION

a = nondimensional growth coefficient case (ii)
c = ratio between wave velocity and $\overline{U}_a$
D = differentiation with respect to y
g = gravitational acceleration
h = film thickness for the unperturbed case
m, n = space coefficient, Equation (3)
P = pressure
Re = Reynolds number = $\overline{U}_a h/\nu \equiv (gh^3 \sin\beta)/3\nu^2$
U_x, U_y, U_z = velocity components in x, y and z direction
$\overline{U}$ = X component of velocity in Nusselt's flow
$\overline{U}_a$ = average velocity of the liquid = $(gh^2 \sin\beta)/3\nu$
u = $U_x/\overline{U}_a$
$\bar{u}$ = $\overline{U}/\overline{U}_a$
v = $U_y/\overline{U}_a$
X, Y, Z = stream-wise, depth, and transverse spatial coordinates
x, y, z = nondimensional spatial coordinates X/h, Y/h, Z/h

Greek Letters

α = stream-wise (case i) or transversal case (ii) wave number
β = angle of plane from horizontal
γ = exponent in the expression of the disturbance
η' = surface perturbation
ν = kinematic viscosity
ρ = density
σ = surface tension
ζ = surface tension group = $\sigma(3/g\rho^3\nu^4\sin\beta)^{1/3}$
$'$ (prime) denotes infinitesimal perturbation quantity
$\wedge$ denotes y dependence of a quantity

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Diffusion of Grouped Multicomponent Mixtures in Uniform and Nonuniform Media

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Many biological and manmade processes involve diffusion of several distinct chemical species. However, it is often inconvenient or impossible to measure experimentally the concentration of each individual species. In such situations a practice sometimes called *grouping, lumping,* or *aggregation* is commonly employed: this involves representation of the mixture by one or more grouped or pseudocomponents which are in fact themselves mixtures. An example of this approach is the grouping together of many compounds into the single pseudocomponent "blood urea nitrogen."

In addition to accommodating experimental difficulties in resolving individual species, use of pseudocomponents reduces the number of variables necessary in the diffusion model. While such model simplification is obviously a laudable outcome, it is important to remember that a cost is also incurred. Models cast in terms of grouped species are rarely exact, as has been shown by several recent studies on the related problem of aggregation in reacting systems (see, for example, Wei and Kuo, 1969; Bailey, 1972; Hutchinson and Luss, 1970; Luss and Hutchinson, 1971; Golikeri and Luss, 1972).

The objective of this work is to explore the impact of lumping on the accuracy of models for multicomponent diffusion in plane sheets, cylinders, and spheres. In particular, it will be shown that use of an average diffusivity obtained from steady state diffusion through a plane sheet usually results in an overestimate of the unsteady diffusion rate for all the geometries mentioned. A similar conclusion is proven for diffusion of a single species through a nonuniform plane sheet. Also, guidelines for choice of grouped species are presented. Both the analysis concept and the particular mathematical devices used here derive directly from the work of Hutchinson and Luss (1970). The following presentation is limited to situations where the transport of each component can be described by the Fick's Law form with constant diffusion coefficient.

DIFFUSION THROUGH A PLANE SHEET

The first diffusion medium to be considered is a homogeneous plane sheet of thickness L which at time zero contains none of the diffusing components of interest. The fluid adjacent to the surface of this sheet at $x = 0$ contains none of the permeating species at all times, while the face at $x = L$ is bathed for time $t \geqq 0$ with fluid containing a mixture of components capable of diffusing through the sheet. It is convenient to index these species according to their diffusivities in the sheet medium. Consequently, $c_e(D)dD$ denotes the external concentration of all compounds with diffusivities between D and $D + dD$. Considering for the moment that all permeating species are to be grouped together into one pseudocomponent p, the concentration of this pseudocomponent at the $x = L$ face of the sheet is given by

$$c_{pe} \triangleq \int_0^\infty c_e(D)dD \tag{1}$$

Under the assumption given above, diffusion of each species through the sheet can be treated independently. Letting $Q(t, D)dD$ be the total amount of permeant with diffusivity between D and $D + dD$ which has passed through a unit area of the $x = L$ face in time t, standard treatments of transient diffusion reveal that (see, for example, Crank (1956), p. 47)

$$Q(t, D)dD = \frac{t}{L} Dc_e(D)dD + \frac{L}{3} c_e(D)dD - \frac{2L}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left[-Dn^2 \pi^2 t/L^2\right] c_e(D)dD \tag{2}$$

The total amount of pseudocomponent $Q_p(t)$ which passed through the $x = L$ face in time t may now be obtained by summing all contributions given by Equation (2) to obtain

$$Q_p(t) \triangleq \int_0^\infty Q(t, D)dD = \frac{D_p}{L} c_{pe}t + \frac{L}{3} c_{pe} - \frac{2L}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \int_0^\infty \exp\left[-Dn^2 \pi^2 t/L^2\right] c_e(D)dD \tag{3}$$

where D_p is an average pseudocomponent diffusivity defined by

$$D_p \triangleq \int_0^\infty Dc_e(D)dD \Bigg/ \int_0^\infty c_e(D)dD \tag{4}$$

Although diffusivities ranging from zero to arbitrarily large have been allowed in the preceding development, in all real situations even the slowest component in the mixture will have a finite diffusivity. This implies that after a sufficiently long time the final term on the right-hand side of Equation (3) will be negligible and that Q_p becomes a linear function of time:

$$Q_{ps}(t) = \frac{D_p}{L} c_{pe}t + \frac{L}{3} c_{pe} \tag{5}$$

At this point steady state has been achieved: the flux through the sheet and all concentration profiles within the sheet are time-invariant. From measurements of $Q_p(t)$ in this steady state regime, D_p may be readily determined providing c_{pe} is known.

Equation (5) is of exactly the same form as applies to a single species. Thus, steady state diffusion of the pseudocomponent through the sheet can be modeled exactly as a single component case providing a suitable pseudocomponent diffusivity is employed. It is important to note in this regard, however, that the pseudocomponent diffusivity D_p in Equation (4) is a function of the permeant ratios in the external solution. Consequently, use of a lumped diffusion model may be inadequate even for steady state processes if the composition at fluid-membrane interface(s) varies significantly from point to point within the process unit. Also, changing the composition of the feed stream to a membrane process will in general result in a concomitant change in pseudocomponent diffusivity in the membrane.

Examination of Equation (3) reveals that detailed knowledge of the external concentration distribution c_e is necessary in order to calculate Q_p exactly in the transient interval preceding steady state. As explained in the introduction, such detailed information is often unavailable. In the absence of complete composition data, the grouping approach suggests that the pseudocomponent be viewed as a pure species during the transient period. Using the diffusivity D_p determined from steady state data in this lumped model gives an approximate cumulative permeant flow through the $x = L$ face of

$$Q_{pA}(t) = \frac{D_p}{L} c_{pe}t + \frac{L}{3} c_{pe} - \frac{2Lc_{pe}}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left[-D_p n^2 \pi^2 t/L^2\right] \tag{6}$$

The error incurred by aggregating all diffusing species into one in the transient model is

$$e(t) \triangleq Q_{pA}(t) - Q_p(t) \tag{7}$$

which can be written using Equations (3) and (6) as

$$e(t) = \frac{2L}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \left\{ \int_0^\infty \exp\left[-Dn^2 \pi^2 t/L^2\right] c_e(D)dD - \exp\left[-D_p n^2 \pi^2 t/L^2\right] c_{pe} \right\} \tag{8}$$

The sign of $e(t)$ is readily determined using the following specialization of an inequality due to Hardy et al. (1934): given a nonnegative weight function $\beta(D)$,

$$\frac{\int_0^\infty \beta(D) \exp\left[-D\tau\right] dD}{\int_0^\infty \beta(D)dD} \geqq \exp\left[\left[\frac{\int_0^\infty D\beta(D)dD}{\int_0^\infty \beta(D)dD}\right] \tau\right] \tag{9}$$

providing the left-hand side exists and is finite. Taking $\beta(D) = c_e(D)$ and $\tau = n^2 \pi^2 t/L^2$ in Inequality (9) shows that the term in brackets on the right-hand side of Equation (9) is nonnegative for every n. Since the coefficients of all bracketed terms in the series are positive, it follows that

$$e(t) \geqq 0 \tag{10}$$

Equality in Condition (10) will apply only when all components have the same diffusivity. Consequently, in a mixture of species with differing diffusivities, lumping always results in an overestimate of the total amount diffused.

Exactly the same logic as just applied can be employed to analyze diffusion of a single species through a plane sheet consisting of several planar regions in which the permeating compound has different diffusivities. Letting $\alpha(D)dD$ denote the fraction of the membrane area in which the permeant has a diffusivity between D and $D + dD$, the total amount of permeant passing through an average unit area of the $x = L$ face is

$$Q_A(t) = \frac{D_A}{L} c_e t - \frac{L}{3} c_e$$

$$- \frac{2Lc_e}{\pi^2} \sum_{n=1}^{\infty} \int_0^{\infty} \alpha(D) \exp\left[- Dn^2 \pi^2 t/L^2\right] dD \quad (11)$$

where c_e is the fluid permeant concentration at the $x = L$ face and D_A is an area-averaged diffusivity:

$$D_A \triangleq \int_0^{\infty} D\alpha(D)dD \quad (12)$$

Again lumping causes relatively few problems in steady state, but transient diffusion cannot be described exactly without detailed knowledge of membrane structure. Proceeding as above, it follows easily that use of D_A in the lumped transient model will overestimate the amount diffused if the membrane is nonuniform.

PERMEANT UPTAKE IN MEDIA OF VARIOUS SHAPES

In many situations the total amount of diffusing species which has entered the diffusion medium is of paramount interest. Examination of Crank's (1956) monograph reveals that the form of the total uptake function is the same for plane sheets, cylinders, spheres, hollow spheres, and several other configurations. Returning now to the problem of multicomponent diffusion in uniform media, the total amount of substance with diffusivities between D and $D + dD$ which enters the medium in time t takes the general form

$$M(t, D)dD = c_e(D)dD \left[a_0 - \sum_{n=1}^{\infty} a_n \, e^{-b_n D t} \right] \quad (13)$$

(a_n, $b_n > 0$, $n = 0, 1, 2, \ldots$) for all the geometries mentioned. Consequently, the amount of all species within the medium at time t is

$$M_p(t) \triangleq \int_0^{\infty} M(t, D)dD$$

$$= a_0 \, c_{pe} - \sum_{n=1}^{\infty} a_n \int_0^{\infty} c_e(D) \, e^{-b_n D t} \, dD \quad (14)$$

The approximate total amount of pseudocomponent with diffusivity D_p taken up is given by

$$M_{pA}(t) = a_0 \, c_{pe} - \sum_{n=1}^{\infty} a_n \, c_{pe} \, e^{-b_n D_p t} \quad (15)$$

Again applying Inequality (9), it follows immediately that

$$M_{pA}(t) - M_p(t) \geqq 0 \quad (16)$$

with equality holding only in the case of equal diffusivities. Hence use of a lumped diffusion model will usually cause an overestimate of the total uptake of the pseudocomponent.

LOWER BOUNDS AND GUIDELINES FOR GROUPING

A lumped diffusion model has in all instances examined above produced an upper bound on mass transport rates. Following Hutchinson and Luss (1970), lower bounds may readily be obtained by noting that

$$- \frac{1}{b_n} \frac{d}{dt} \int_0^{\infty} c_e(D) \, e^{-b_n D t} \, dD$$

$$= \int_0^{\infty} Dc_e(D) \, e^{-b_n D t} \, dD \geqq m_1 e^{-b_n t m_2/m_1} \quad (17)$$

where m_k denotes the kth moment of $c_e(D)$:

$$m_k \triangleq \int_0^{\infty} D^k \, c_e(D)dD \quad (18)$$

Inequality (17) follows from (9) with $\beta(D) = Dc_e(D)$ and $\tau = b_n t$. By integrating (17) and substituting the result in the expressions above for Q_p and M_p, lower bounds are obtained. For the sake of brevity these straightforward calculations will not be reported here.

Often it will not be necessary nor desirable to aggregate all diffusing species into one lump. By examining the difference between the upper and lower bounds given above, one concludes that maximum errors are minimized by grouping together into pseudocomponents those species whose diffusivities are most alike.

Additional results such as refined bounds, realizability of bounds, and related matters of interest for this problem could be developed by more parallels of the Hutchinson-Luss (1970) strategy. These will not be pursued further here, where the intent is to sew the first threads tying their approach to diffusion problems. With this now accomplished, it is relatively easy to extend the fabric of the theory.

NOTATION

a_k, b_k = positive constants
c = concentration
D = diffusivity
e = error
L = thickness of plane sheet
M = total amount of a permeant in diffusion medium
m_k = moment defined in Equation (18)
Q = total amount of permeant which has diffused through face at $x = L$
t = time
x = position coordinate in plane sheet

Greek Letters

α = area distribution function
β = nonnegative weight function

Subscripts

A = approximate result from lumped model
A = area averaged quantity
e = at $x = L$ face of plane sheet or at outer surface of other shapes
p = pseudocomponent consisting of all diffusing species

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