Dispersion, Mass Transfer and Chemical Reaction in Multiphase Contactors

Part I: Theoretical Developments

T. A. HATTON and
E. N. LIGHTFOOT

Department of Chemical Engineering
University of Wisconsin
Madison, WI 53706

The convective dispersion theory of Gill and Sankarasubramanian is extended to allow for multiphase mass transfer interactions in column-type contactors, and for multisolute, reversible and irreversible, homogeneous and wall-catalyzed heterogeneous chemical reactions in the individual phases. This theory can now be applied in any transverse average, not just the area average used in the past, and additional interactions between the phases not normally accounted for in the traditional axial dispersion model are indicated.

SCOPE

The adverse effect of longitudinal mixing on mass transfer in continuous contact, multiphase equipment is now well documented. Nevertheless, there are still many facets of the dispersion process that are not yet adequately understood, a prime example being the differences in the dispersion parameter values obtained from dispersion experiments when a soluble rather than an inert tracer is used (Hatton and Woodburn, 1978; Linek et al., 1978). Through an extension of the generalized dispersion theory of Gill and Sankarasubramanian (1970, 1971), it was recently shown that the hydrodynamic and mass transfer interactions between the phases can have a significant effect on the dispersion coefficients for the individual phases (Hatton and Lightfoot, 1982). Only interphase mass transfer was considered, however, and no account was taken of the possible effects of chemical reaction on these parameters. This restriction has now been removed and the developments presented here allow not only for homogeneous chemical reactions in the individual phases, but also for wall-catalyzed, heterogeneous reactions. All reactions are assumed to be of first order, and may be either reversible or irreversible.

CONCLUSIONS AND SIGNIFICANCE

The mathematical developments reported here extend the convective dispersion theory of Gill and Sankarasubramanian (1970, 1971) to multiphase (or multisolute) systems, and now permit this theory to be applied in any transverse average, not just the area average used in the past. Moreover, both homogeneous and heterogeneous, wall-catalyzed reactions are readily handled using this theory, allowing an assessment to be made of the effect of chemical and mass transfer interactions on the dispersion characteristics of the individual phases or species. A numerical study based on the theoretical results obtained in this work is given in Part II.

INTRODUCTION

Despite the fact that two-phase flow processes form the overwhelming bulk of all the operations carried out in the petrochemical and allied industries, it would appear that dependable strategies for scale-up from laboratory or pilot-plant runs, and for process optimization, are, in the main, still lacking. The extension of the traditional plug-flow model to allow for the adverse effects of longitudinal mixing on the mass transfer performance of multiphase contactors has, to some extent, alleviated this problem. However, one is still faced with the often inconsistent and unreliable experimental data reported in the literature for the dispersion and mass transfer parameters appearing in the model descriptions. For gas-liquid operations in packed beds, for instance, it would seem that much has still to be done before the dispersion processes have been sufficiently well-characterized for confident inclusion in design procedures, whereas for mechanically agitated systems there is still no clear consensus even as to the relative importance of mixing in the dispersed phase *vis-a-vis* that in the continuous phase (Hatton, 1981).

Although there is a large body of literature on the experimental evaluation of dispersion coefficients in process equipment, surprisingly little attention has been paid to uncovering the underlying structure of these coefficients through detailed mathematical analyses of the hydrodynamic and physico-chemical characteristics of the systems under consideration. Yet, in light of the large-scale deviations from ideal plug flow known to persist in industrial installations, it would seem that it is precisely these flow maldistribution effects that should be entertained before any further progress can be anticipated in the quantitative interpretation and prediction of column behavior. It was in an attempt to better understand these phenomena that Hatton and Lightfoot (1982) extended the generalized dispersion theory of Gill and Sankarasubramanian (1970, 1971) to two-phase, counter-current mass transfer systems. They found that interphase mass transfer interactions can affect the dispersion characteristics of the individual phases significantly, and that care should be exercised in using published dispersion data for design purposes. Their analysis was restricted to the transfer of a single, nonreactive solute.

In many industrially significant separation processes the transferred species is reacted with a suitable reagent in the receiving phase to either enhance the rate of mass transfer or to improve the selectivity of the process for one soluble component over another.

Correspondence concerning this paper should be addressed to T. A. Hatton, Department of Chemical Engineering, M.I.T., Cambridge, MA 02139.

Common examples are the absorption of carbon dioxide by amine solutions, and the selective removal of hydrogen sulfide from H_2S-CO_2 mixtures, also using amine solutions. In other applications, promotion of the chemical reaction itself is the primary reason for bringing the phases together, as in the slurry and trickle-bed reactors used in industrial hydrogenation and polymerisation processes.

Popular accounts of interphase mass transfer accompanied by chemical reaction (Astarita, 1967; Danckwerts, 1970) make only passing reference to the design of countercurrent contactors using the axial dispersion model, and even then it is tacitly assumed that dispersion coefficients estimated from intraphase studies are directly applicable under reactive mass transfer conditions. Since it is now known that simple mass transfer interactions can, to a large extent, affect the dispersion processes, it is to be anticipated that the added complication of chemical interactions may also have a pronounced effect on the dispersion characteristics of the individual phases. It is our purpose here to investigate this conjecture, and we do so through a further extension of the generalized dispersion theory of Gill and Sankarasubramanian (1970, 1971) to allow also for reactive solutes.

A related problem is that of the convective dispersion of a mixture of reactants which can undergo either homogeneous chemical transformation or wall-catalyzed heterogeneous reaction, or both. Again, the problem is one of suitably describing the axial dispersion characteristics of the system in terms of a one-dimensional dispersed plug-flow model. While much progress has been made in this regard for single-solute systems (Sankarasubramanian and Gill, 1973, 1974; Subramanian et al., 1974; Gill, 1975; Fife and Nicholes, 1975; De Gance and Johns, 1978), currently available results on multisolute interactions are limited either in their scope, or in their general applicability.

Johns and De Gance (1975) used Taylor-type reasoning to develop expressions for the effective solute velocities and dispersion coefficients for multicomponent diffusion-reaction systems. However, for single-solute systems, Subramanian et al. (1974) concluded that such intuitive arguments may fail when extended beyond their original framework, and hence it would seem that the Johns and De Gance results must be approached with some caution. Indeed, the work of Aris (1980) on the dispersion of solutes undergoing consecutive irreversible reactions supports this contention, and he has commented on the need for further investigation into multisolute reaction systems. De Gance and Johns (1980) have subsequently presented some results on diffusional interactions, although only for a restricted set of conditions.

In this paper, we extend our earlier analysis (Hatton and Lightfoot, 1982) to include multiphase (or multisolute) interactions, allowing for homogeneous and heterogeneous, reversible and irreversible, first-order chemical reactions, assuming isothermal conditions throughout. We begin by describing a general mathematical model of continuous contact, multiphase reactors which explicitly accounts for the possible existence of large-scale flow maldistribution effects, and we show how this model, and the single-phase, multisolute problem, can be handled within the same mathematical framework. The importance of the concentration-averaging procedures used in the experimental determination of dispersion coefficients is discussed next, followed by a multiphase generalization of Gill and Sankarasubramanian's (1970) convective dispersion theory, in which we allow for arbitrary transverse averaging, which may differ from one phase to the next. The paper concludes with a discussion of the qualitative observations that can be made based on the results of our analysis. Specific numerical examples are reported in a companion paper (Hatton and Lightfoot, 1983).

MATHEMATICAL MODEL OF MULTIPHASE REACTORS

Axial mixing in multiphase contactors can be affected by a hierarchy of dispersion processes which, broadly speaking, may be classified according to the distance scales over which they act. The two processes of primary concern to us here are the convective dispersion effects, caused by large-scale velocity nonuniformities, and the turbulent eddy processes, which act locally over distances on the order of the characteristic eddy sizes, or packing particle dimensions. The lateral turbulent mixing is responsible for a partial mitigation of the radial concentration profile distortions caused by the convective nonuniformities, and this gives rise to the well-known phenomenon of Taylor dispersion. It is this effect that is normally observed in tracer tests for determining axial dispersion coefficients, and it is therefore important that these interactions between the large-scale flow maldistributions and the lateral turbulent mixing be accommodated in any realistic investigation of the structure of the axial dispersion coefficients routinely measured in laboratory and pilot-scale tests.

Mathematical descriptions of multiphase contactors are usually based on the pseudocontinuum approximation, wherein all phases are supposed to coexist at every point within the contactor, and the fine details of the local phase distributions are ignored. Such an approach is eminently suitable for our modelling purposes, since the flow maldistribution and channelling effects can then be described in terms of nonuniform velocity profiles, taken to be continuous functions of radial position, and the turbulent eddy mixing can be likened to a diffusion-type process, characterized by eddy diffusion coefficients for each phase. While it is probable that these parameters will depend on the local hydrodynamic conditions, in the interests of mathematical tractability we assume them to be everywhere constant, independent of position. However, the local dispersion processes will, in general, be anisotropic, and hence the parameters for any given phase will differ depending on whether they describe dispersion parallel with or normal to the primary flow direction.

Any solute that is distributed between two or more phases will be treated as a different species within each phase, so that interphase mass transfer, characterized in the customary manner through an overall mass transfer coefficient, can be looked upon as a reversible, first-order chemical reaction, the mass transfer coefficient playing the role of the reaction rate constant. Hence, in our analysis we do not distinguish between actual interphase chemical reactions and the interphase mass transfer processes—mathematically they are equivalent. Irreversible reactions are readily accommodated in the reaction scheme if it is recognized that the principle of microscopic reversibility precludes the feedback of any subsequent reaction products to the reaction scheme under consideration. Hence these reaction products can be ignored in setting up the problem statement. For simplicity, we assume that none of the reactants participating in the reversible reaction scheme is itself the product of an irreversible reaction.

With this set of assumptions, the material balance equations for a differential element of the contactor can be expressed in matrix notation as

$$\boldsymbol{\epsilon}\frac{\partial \boldsymbol{c}}{\partial t} + \boldsymbol{v}(r)\frac{\partial \boldsymbol{c}}{\partial z} - \boldsymbol{D}_z\frac{\partial^2 \boldsymbol{c}}{\partial z^2} - \boldsymbol{D}_r\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial \boldsymbol{c}}{\partial r}\right) - \boldsymbol{R}'\boldsymbol{c} = \boldsymbol{0} \qquad (1)$$

with radial boundary conditions reflecting symmetry about the column center, and an impermeable (or inert) wall, respectively:

$$\frac{\partial \boldsymbol{c}}{\partial r} = \boldsymbol{0} \qquad \text{at } r = 0 \qquad \text{and } r = R_c \qquad (2)$$

Here, $\boldsymbol{c}$ is the vector of solute concentrations, $\boldsymbol{\epsilon}$ is the matrix of fractional holdup ratios for the individual phases, and $\boldsymbol{v}(r)$ is the matrix of velocity profiles corresponding to these phases. The matrices $\boldsymbol{D}_z$ and $\boldsymbol{D}_r$ contain the axial and radial eddy diffusion coefficients, respectively. These matrices are all diagonal. The matrix of reaction rate constants $\boldsymbol{R}'$ is comprised of two parts, one ($\boldsymbol{R}'_{\text{rev}}$) corresponding to the reversible reaction schemes, and the other ($\boldsymbol{R}'_{\text{irr}}$) being the diagonal matrix of reaction rate constants for the irreversible solute degradation reactions. The elements of $\boldsymbol{R}'_{\text{rev}}$ must satisfy $r_{ij} \geq 0$ for $i \neq j$, and

$$r_{ii} = -\sum_{\substack{j=1 \\ j\neq i}}^{N} r_{ji} \qquad (3)$$

where N is the number of species considered.

In the absence of nonlinear effects, Eqs. 1 and 2 constitute a fairly general model of multiphase separations processes and reactors of the slurry and trickle-bed type, and can be used in conjunction with a generalized dispersion theory to investigate the axial dispersion characteristics of such contactors. Here, we will be concerned only with the initial distribution, or pulse dispersion problem, since, for linear systems, this gives the fundamental solution from which the results for all other classes of problems may be generated through superpositioning arguments. The procedures we follow require that we assume a doubly infinite column in our analysis, and it is for this reason that we have refrained from specifying axial boundary conditions in the problem statement. For cocurrent reactors, this should pose no undue difficulties since the solute will, for the most part, move downstream from the point of injection, and will not see the upstream regions. Hence, in such cases it is immaterial whether or not the system is finite. Unfortunately, similar considerations do not apply under countercurrent flow conditions, since solute is able to move upstream from its point of injection and can be removed from the system permanently. As a result, the development of the solute pulse with time for counterflow systems will certainly be affected by the lack of suitable finite axial boundaries. Nevertheless, it is felt that even though our countercurrent results will not be truly representative of the actual processes under consideration, they will contribute significantly to our understanding of the convective dispersion phenomena in such systems.

A second class of problems, related to the one just discussed, is that in which there are multiple chemical reactions occurring simultaneously in a single-phase tubular reactor. These reactions may be either homogeneous in the bulk of the fluid or heterogeneous at the tube wall. Again, both reversible and irreversible reaction schemes are allowed for, subject of course to the usual linearity restrictions. This problem is characterized by a single velocity $v(r)$ for all species, and its mathematical statement is

$$\frac{\partial \boldsymbol{c}}{\partial t} + v(r)\frac{\partial \boldsymbol{c}}{\partial z} - \boldsymbol{\mathcal{D}}\left[\frac{\partial^2 \boldsymbol{c}}{\partial z^2} + \frac{1}{r}\frac{\partial}{\partial r}r\frac{\partial \boldsymbol{c}}{\partial r}\right] - \boldsymbol{R}'\boldsymbol{c} = 0 \qquad (4)$$

$$\frac{\partial \boldsymbol{c}}{\partial r} = 0 \qquad \text{at } r = 0 \qquad (5)$$

$$\boldsymbol{\mathcal{D}}\frac{\partial \boldsymbol{c}}{\partial r} + \boldsymbol{K}'\boldsymbol{c} = 0 \qquad \text{at } r = R_c \qquad (6)$$

where $\boldsymbol{\mathcal{D}}$ is a diagonal matrix of molecular diffusion coefficients, and $\boldsymbol{K}'$, like $\boldsymbol{R}'$, is a matrix of reaction rate constants for both reversible and irreversible reactions pathways. [We explicitly exclude the possibility of the diffusional interactions between the species implied by a more general matrix $\boldsymbol{\mathcal{D}}$. DeGance and Johns (1980), allowed for a diffusional coupling between the species, but only for the nonreactive problem. Indeed, when heterogeneous wall reactions were accommodated in their model, they found it necessary to restrict their $\boldsymbol{\mathcal{D}}$-matrix such that $\boldsymbol{\mathcal{D}} = \mathcal{D}\boldsymbol{I}$. This restriction is not necessary in the developments that follow.] The elements of $\boldsymbol{K}_{\text{rev}}$ must satisfy $k_{ij} \geq 0$ for $i \neq j$ and

$$k_{ii} = -\sum_{\substack{j=1\\j\neq i}}^{N} k_{ji} \qquad (7)$$

The similarity between Eqs. 1 and 2 and Eqs. 4 through 6 is obvious, and, indeed, both sets of equations are special cases of the more general problem

$$\boldsymbol{\epsilon}\frac{\partial \boldsymbol{c}}{\partial \tau} + \boldsymbol{V}(r)\frac{\partial \boldsymbol{c}}{\partial \zeta} - \boldsymbol{P}_{\zeta}^{-1}\frac{\partial^2 \boldsymbol{c}}{\partial \zeta^2} - \boldsymbol{P}_{\eta}^{-1}\frac{1}{\eta}\frac{\partial}{\partial \eta}\left(\eta\frac{\partial \boldsymbol{c}}{\partial \eta}\right) - \boldsymbol{R}\boldsymbol{c} = 0 \qquad (8)$$

$$\frac{\partial \boldsymbol{c}}{\partial \eta} = 0 \qquad \text{at } \eta = 0 \qquad (9)$$

$$\boldsymbol{P}_{\eta}^{-1}\frac{\partial \boldsymbol{c}}{\partial \eta} + \boldsymbol{K}\boldsymbol{c} = 0 \qquad \text{at } \eta = 1 \qquad (10)$$

Here, all dimensional quantities have been suitably scaled by defining the dimensionless variables

$$\tau = tu_r/R_c; \quad \zeta = z/R_c; \quad \eta = r/R_c$$

$$\boldsymbol{V}(r) = \frac{1}{u_r}\,\boldsymbol{v}(r); \quad \boldsymbol{P}_{\zeta}^{-1} = \frac{1}{u_rR_c}\,\boldsymbol{D}_z; \quad \boldsymbol{P}_{\eta}^{-1} = \frac{1}{u_rR_c}\,\boldsymbol{D}_r$$

$$\boldsymbol{R} = \frac{R_c}{u_r}\,\boldsymbol{R}'; \quad \boldsymbol{K} = \frac{R_c}{u_r}\,\boldsymbol{K}'$$

where u_r is some reference velocity.

It is perhaps worthwhile to note at this point that the multiphase reactor problem is recovered by setting $\boldsymbol{K} = 0$, whereas for the tubular reactor we must have $\boldsymbol{\epsilon} = \boldsymbol{I}$ and $\boldsymbol{V}(r) = v(r)\boldsymbol{I}/u_r$.

DEVELOPMENT OF THE AXIAL DISPERSION MODEL

The traditional description of mass transfer and chemical reaction in multiphase contactors is in terms of the one-dimensional axial dispersion model, which approximates the axial variations in, and temporal evolution of, the average concentrations of the individual species and phases. For initial distribution problems, this model can be put on a more rigorous footing using the detailed two-dimensional model introduced above, and a multiphase generalization of the convective dispersion theory of Gill and Sankarasubramanian (1970, 1971).

The average concentrations measured during dispersion experiments depend on the means of solute detection (e.g., cup-mixing, area and radial average concentrations have all been used, as have point concentration values) and, indeed, for multiphase systems the averaging procedures used may differ from one phase to another. Thus, while in actual process operations the cup-mixing or flow-average concentration of each phase may be of most interest, we should, nevertheless, also address the problem of other, arbitrary transverse averaging. To do this, we introduce a diagonal matrix $\boldsymbol{\omega}(\eta)$ of weighting functions which reflect the different concentration measurement techniques for the individual phases. [For instance, if cup-mixing averages are desired, $\boldsymbol{\omega}(\eta) = \langle \boldsymbol{V}\rangle^{-1}\boldsymbol{V}$, whereas for area averages $\boldsymbol{\omega}(\eta)$ is given by the identity matrix. Note that $\boldsymbol{\omega}(\eta)$ should be normalized such that $\langle\boldsymbol{\omega}\rangle = \boldsymbol{I}$.] We also define an average species concentration vector $\boldsymbol{c}_m$ by

$$\boldsymbol{c}_m = 2\int_0^1 \eta\boldsymbol{\omega}\boldsymbol{c}\,d\eta = \langle\boldsymbol{\omega}\boldsymbol{c}\rangle = \{\boldsymbol{c}\} \qquad (11)$$

Equation 11 also serves to define the averages denoted by $\langle\cdot\rangle$ (the area average) and $\{\cdot\}$.

Our first step in the development of the axial dispersion model is to take the appropriate average of Eq. 8 by multiplying through by $2\eta\boldsymbol{\omega}(\eta)$ and integrating over η from 0 to 1. We obtain

$$\boldsymbol{\epsilon}\frac{\partial}{\partial \tau}\,\boldsymbol{c}_m - \boldsymbol{P}_{\zeta}^{-1}\frac{\partial^2}{\partial \zeta^2}\,\boldsymbol{c}_m - \boldsymbol{R}\boldsymbol{c}_m - \langle\boldsymbol{\Delta}\boldsymbol{c}\rangle + \frac{\partial}{\partial \zeta}\{\boldsymbol{V}\boldsymbol{c}\}$$
$$- \boldsymbol{P}_{\eta}^{-1}\langle(\nabla^2\boldsymbol{\omega})\boldsymbol{c}\rangle + 2\left[\boldsymbol{\omega}\boldsymbol{K}\boldsymbol{c} + \boldsymbol{P}_{\eta}^{-1}\frac{d\boldsymbol{\omega}}{d\eta}\,\boldsymbol{c}\right]_{\eta=1} = 0 \qquad (12)$$

where

$$\boldsymbol{\Delta} = \boldsymbol{\omega}\boldsymbol{R} - \boldsymbol{R}\boldsymbol{\omega}$$

and

$$(\nabla^2\boldsymbol{\omega}) = \frac{1}{\eta}\frac{d}{d\eta}\left(\eta\frac{d}{d\eta}\,\boldsymbol{\omega}\right)$$

At this point, it would appear that we are at an impasse because, while it is our purpose to develop a one-dimensional description in terms of the average concentration $\boldsymbol{c}_m$ only, a number of the terms in Eq. 12 cannot be related directly to $\boldsymbol{c}_m$. Indeed, this is a problem common to all convective dispersion studies, and the procedures developed by Aris (1956), Gill and Sankarasubramanian (1970, 1971) and DeGance and Johns (1978) for single-phase systems are all attempts to circumvent this difficulty. Here, we extend the ideas put forward by Gill and Sankarasubramanian (1970), and postulate that the concentration vector $\boldsymbol{c}$ can be expanded in terms of a suitably defined average concentration, $\boldsymbol{\theta}_m$, and its axial derivatives. Thus

$$\boldsymbol{c} = \sum_{k=0}^{\infty}\phi_k(\eta,\tau)\frac{\partial^k\theta_m}{\partial\zeta^k} = \sum_{k=0}^{\infty}\boldsymbol{\Phi}_k(\eta,\tau)\frac{\partial^k\boldsymbol{\theta}_m}{\partial\zeta^k} \qquad (13)$$

where

$$\boldsymbol{\theta}_m = \theta_m \mathbf{1} \qquad \text{and } \boldsymbol{\Phi}_k = \operatorname{diag}(\phi_k^{(1)}, \ldots, \phi_k^{(N)})$$

Gill (1969) and Hatton and Lightfoot (1982) used a similar expansion in their analyses of two phase, interacting flow systems, using as θ_m the area-average concentration taken over both phases. Here, however, we use a different definition for θ_m which, for the moment, we assume to be known, preferring to leave the discussion of its explicit form until later.

With the expansion (Eq. 13) we have

$$\boldsymbol{c}_m = \{\boldsymbol{\Phi}_0\}\boldsymbol{\theta}_m + \{\boldsymbol{\Phi}_1\}\frac{\partial \boldsymbol{\theta}_m}{\partial \zeta} + \{\boldsymbol{\Phi}_2\}\frac{\partial^2 \boldsymbol{\theta}_m}{\partial \zeta^2} + \sum_{k=3}^{\infty}\{\boldsymbol{\Phi}_k\}\frac{\partial^k \boldsymbol{\theta}_m}{\partial \zeta^k}$$

$$\frac{\partial \boldsymbol{c}_m}{\partial \zeta} = \{\boldsymbol{\Phi}_0\}\frac{\partial \boldsymbol{\theta}_m}{\partial \zeta} + \{\boldsymbol{\Phi}_1\}\frac{\partial^2 \boldsymbol{\theta}_m}{\partial \zeta^2} + \sum_{k=3}^{\infty}\{\boldsymbol{\Phi}_{k-1}\}\frac{\partial^k \boldsymbol{\theta}_m}{\partial \zeta^k}$$

$$\frac{\partial^2 \boldsymbol{c}_m}{\partial \zeta^2} = \{\boldsymbol{\Phi}_0\}\frac{\partial^2 \boldsymbol{\theta}_m}{\partial \zeta^2} + \sum_{k=3}^{\infty}\{\boldsymbol{\Phi}_{k-2}\}\frac{\partial^k \boldsymbol{\theta}_m}{\partial \zeta^k}$$

which equations can now be solved for $\boldsymbol{\theta}_m$, $\partial\boldsymbol{\theta}_m/\partial\zeta$ and $\partial^2\boldsymbol{\theta}_m/\partial\zeta^2$ in terms of $\boldsymbol{c}_m$, $\partial\boldsymbol{c}_m/\partial\zeta$, $\partial^2\boldsymbol{c}_m/\partial\zeta^2$ and $\partial^k\boldsymbol{\theta}_m/\partial\zeta^k$ (for $k \geq 3$).

$$\begin{aligned}\boldsymbol{\theta}_m = {} & \{\boldsymbol{\Phi}_0\}^{-1}\boldsymbol{c}_m - \{\boldsymbol{\Phi}_0\}^{-2}\{\boldsymbol{\Phi}_1\}\frac{\partial \boldsymbol{c}_m}{\partial \zeta} - \{\boldsymbol{\Phi}_0\}^{-3}[\{\boldsymbol{\Phi}_0\}\{\boldsymbol{\Phi}_2\} \\ & - \{\boldsymbol{\Phi}_1\}^2]\frac{\partial^2 \boldsymbol{c}_m}{\partial \zeta^2} - \{\boldsymbol{\Phi}_0\}^{-3}\sum_{k=3}^{\infty}[\{\boldsymbol{\Phi}_1\}^2\{\boldsymbol{\Phi}_{k-2}\} - \{\boldsymbol{\Phi}_1\}\{\boldsymbol{\Phi}_0\}\{\boldsymbol{\Phi}_{k-1}\} \\ & - \{\boldsymbol{\Phi}_0\}\{\boldsymbol{\Phi}_2\}\{\boldsymbol{\Phi}_{k-2}\} + \{\boldsymbol{\Phi}_0\}^2\{\boldsymbol{\Phi}_k\}]\frac{\partial^k \boldsymbol{\theta}_m}{\partial \zeta^k}\end{aligned} \tag{14}$$

$$\begin{aligned}\frac{\partial \boldsymbol{\theta}_m}{\partial \zeta} = {} & \{\boldsymbol{\Phi}_0\}^{-1}\frac{\partial \boldsymbol{c}_m}{\partial \zeta} - \{\boldsymbol{\Phi}_0\}^{-2}\{\boldsymbol{\Phi}_1\}\frac{\partial^2 \boldsymbol{c}_m}{\partial \zeta^2} \\ & + \{\boldsymbol{\Phi}_0\}^{-2}\sum_{k=3}^{\infty}[\{\boldsymbol{\Phi}_1\}\{\boldsymbol{\Phi}_{k-2}\} - \{\boldsymbol{\Phi}_0\}\{\boldsymbol{\Phi}_{k-1}\}]\frac{\partial^k \boldsymbol{\theta}_m}{\partial \zeta^k}\end{aligned} \tag{15}$$

$$\frac{\partial^2 \boldsymbol{\theta}_m}{\partial \zeta^2} = \{\boldsymbol{\Phi}_0\}^{-1}\frac{\partial^2 \boldsymbol{c}_m}{\partial \zeta^2} - \{\boldsymbol{\Phi}_0\}^{-1}\sum_{k=3}^{\infty}\{\boldsymbol{\Phi}_{k-2}\}\frac{\partial^k \boldsymbol{\theta}_m}{\partial \zeta^k} \tag{16}$$

On substituting Eqs. 13 through 16 in Eq. 12, and defining

$$\boldsymbol{\Upsilon}_i = -\langle \boldsymbol{\Delta\Phi}_i\rangle - \boldsymbol{P}_\eta^{-1}\langle \boldsymbol{\Phi}_i \nabla^2 \boldsymbol{\omega}\rangle + 2\left[\boldsymbol{\omega K} + \boldsymbol{P}_\eta^{-1}\frac{d\boldsymbol{\omega}}{d\eta}\right]_{\eta=1}\boldsymbol{\Phi}_i\bigg|_{\eta=1}$$

we can show, after some algebraic rearrangement, that

$$\begin{aligned}\boldsymbol{\epsilon}\frac{\partial \boldsymbol{c}_m}{\partial \tau} & + [\{\boldsymbol{V\Phi}_0\} - \boldsymbol{\Upsilon}_0\{\boldsymbol{\Phi}_1\}\{\boldsymbol{\Phi}_0\}^{-1} + \boldsymbol{\Upsilon}_1]\{\boldsymbol{\Phi}_0\}^{-1}\frac{\partial \boldsymbol{c}_m}{\partial \zeta} \\ & - [\boldsymbol{P}_\zeta^{-1} + (\{\boldsymbol{V\Phi}_0\}\{\boldsymbol{\Phi}_1\} - \{\boldsymbol{V\Phi}_1\}\{\boldsymbol{\Phi}_0\})\{\boldsymbol{\Phi}_0\}^{-2} + \boldsymbol{\Upsilon}_0(\{\boldsymbol{\Phi}_0\}\{\boldsymbol{\Phi}_2\} \\ & - \{\boldsymbol{\Phi}_1\}^2)\{\boldsymbol{\Phi}_0\}^{-3} + \boldsymbol{\Upsilon}_1\{\boldsymbol{\Phi}_1\}\{\boldsymbol{\Phi}_0\}^{-2} - \boldsymbol{\Upsilon}_2\{\boldsymbol{\Phi}_0\}^{-1}]\frac{\partial^2 \boldsymbol{c}_m}{\partial \zeta^2} \\ & - [\boldsymbol{R} - \boldsymbol{\Upsilon}_0\{\boldsymbol{\Phi}_0\}^{-1}]\boldsymbol{c}_m = \sum_{k=3}^{\infty}(\{\boldsymbol{V\Phi}_0\}[\{\boldsymbol{\Phi}_0\}\{\boldsymbol{\Phi}_{k-1}\} - \{\boldsymbol{\Phi}_1\}\{\boldsymbol{\Phi}_{k-2}\}] \\ & + [\{\boldsymbol{V\Phi}_1\}\{\boldsymbol{\Phi}_{k-2}\} - \{\boldsymbol{V\Phi}_{k-1}\}\{\boldsymbol{\Phi}_0\}]\{\boldsymbol{\Phi}_0\} + \boldsymbol{\Upsilon}_0[\{\boldsymbol{\Phi}_1\}^2\{\boldsymbol{\Phi}_{k-2}\} \\ & - \{\boldsymbol{\Phi}_1\}\{\boldsymbol{\Phi}_0\}\{\boldsymbol{\Phi}_{k-1}\} - \{\boldsymbol{\Phi}_0\}\{\boldsymbol{\Phi}_2\}\{\boldsymbol{\Phi}_{k-2}\} + \{\boldsymbol{\Phi}_0\}^2\{\boldsymbol{\Phi}_k\}]\{\boldsymbol{\Phi}_0\}^{-1} \\ & + \boldsymbol{\Upsilon}_1[\{\boldsymbol{\Phi}_0\}\{\boldsymbol{\Phi}_{k-1}\} - \{\boldsymbol{\Phi}_1\}\{\boldsymbol{\Phi}_{k-2}\}] + \boldsymbol{\Upsilon}_2\{\boldsymbol{\Phi}_0\}\{\boldsymbol{\Phi}_{k-2}\} \\ & - \boldsymbol{\Upsilon}_k\{\boldsymbol{\Phi}_0\}^2)\{\boldsymbol{\Phi}_0\}^{-2}\frac{\partial^k \boldsymbol{\theta}_m}{\partial \zeta^k}\end{aligned} \tag{18}$$

or

$$\boldsymbol{\epsilon}\frac{\partial \boldsymbol{c}_m}{\partial \tau} + \boldsymbol{\mathsf{V}}\frac{\partial \boldsymbol{c}_m}{\partial \zeta} - \boldsymbol{\mathsf{P}}^{-1}\frac{\partial^2 \boldsymbol{c}_m}{\partial \zeta^2} - \boldsymbol{\mathsf{R}}\boldsymbol{c}_m = \sum_{k=3}^{\infty}\boldsymbol{\mathsf{c}}_k\frac{\partial^k \theta_m}{\partial \zeta^k} \tag{19}$$

where

$$\boldsymbol{\mathsf{R}} = \boldsymbol{R} - \boldsymbol{\Upsilon}_0\{\boldsymbol{\Phi}_0\}^{-1} \tag{20}$$

$$\boldsymbol{\mathsf{V}} = [\{\boldsymbol{V\Phi}_0\} - \boldsymbol{\Upsilon}_0\{\boldsymbol{\Phi}_1\}\{\boldsymbol{\Phi}_0\}^{-1} + \boldsymbol{\Upsilon}_1]\{\boldsymbol{\Phi}_0\}^{-1} \tag{21}$$

and

$$\begin{aligned}\boldsymbol{\mathsf{P}}^{-1} = {} & \boldsymbol{P}_\zeta^{-1} + [\{\boldsymbol{V\Phi}_0\}\{\boldsymbol{\Phi}_1\} - \{\boldsymbol{V\Phi}_1\}\{\boldsymbol{\Phi}_0\}]\{\boldsymbol{\Phi}_0\}^{-2} + \boldsymbol{\Upsilon}_0[\{\boldsymbol{\Phi}_0\}\{\boldsymbol{\Phi}_2\} \\ & - \{\boldsymbol{\Phi}_1\}^2]\{\boldsymbol{\Phi}_0\}^{-3} + \boldsymbol{\Upsilon}_1\{\boldsymbol{\Phi}_1\}\{\boldsymbol{\Phi}_0\}^2 - \boldsymbol{\Upsilon}_2\{\boldsymbol{\Phi}_0\}^{-1}\end{aligned} \tag{22}$$

It is of interest to note that in the above results the matrices $\boldsymbol{\Upsilon}_i$ are, in general, nondiagonal, and hence do not commute with the other matrices, all of which are diagonal. The additional interactions between the species indicated by the general form of the $\boldsymbol{\Upsilon}_i$ are a result of not only the heterogeneous wall reactions, but also arise when different transverse averaging procedures are adopted for the individual phases.

Now, for single-phase systems Gill and Sankarasubramanian (1971) demonstrated that the leading coefficient in the summation term is at least two orders of magnitude smaller than the coefficient of the second order axial derivative terms, and that, to a good approximation, the terms containing third order and higher derivatives of θ_m could be discarded. Hence, following their example, and neglecting the entire righthand side of Eq. 19, we recognize that our result resembles the familiar axial dispersion model frequently used in tracer studies. Furthermore, the structure of the model parameters $\boldsymbol{\mathsf{R}}$, $\boldsymbol{\mathsf{V}}$ and $\boldsymbol{\mathsf{P}}^{-1}$ can be determined explicitly on identification of the expansion coefficients $\boldsymbol{\phi}_0$, $\boldsymbol{\phi}_1$ and $\boldsymbol{\phi}_2$, and this is to be the purpose of the next few sections. We begin by introducing a differential operator which arises naturally in the problem formulation, and whose spectral properties play a crucial role in the identification of θ_m, and in the solution of the differential equations for the coefficients $\boldsymbol{\phi}_k$.

SELF-ADJOINT OPERATOR

We consider the operator

$$\boldsymbol{L} \equiv \boldsymbol{\epsilon}^{-1}\left[\boldsymbol{P}_\eta^{-1}\frac{1}{\eta}\frac{d}{d\eta}\left(\eta\frac{d}{d\eta}\right) + \boldsymbol{R}\right] \tag{23}$$

with domain

$$\left\{x : \frac{dx}{d\eta} = 0 \quad \text{at } \eta = 0; \quad \boldsymbol{P}_\eta^{-1}\frac{dx}{d\eta} + \boldsymbol{K}x = 0 \quad \text{at } \eta = 1\right\} \tag{24}$$

and, looking ahead, we note that the successful determination of θ_m, and the expansion of the $\boldsymbol{\phi}_k$ in terms of the eigenfunctions of this operator, rest on the proper identification of a suitable inner product between any two N-dimensional vector functions within the domain of $\boldsymbol{L}$ under which the self-adjointedness of $\boldsymbol{L}$ is assured. This in turn ensures that all the eigenvalues of the operator are real, and that the eigenfunctions are orthogonal. Our problem, then, is to determine a diagonal weighting matrix $\boldsymbol{W}$ such that under the inner product

$$\langle x,y\rangle = 2\int_0^1 \eta x^T \boldsymbol{\epsilon} \boldsymbol{W} y\, d\eta \tag{25}$$

the operator L satisfies

$$\langle \boldsymbol{L}x,y\rangle - \langle x,\boldsymbol{L}y\rangle = 0 \tag{26}$$

We begin by writing Eq. 26 in full,

$$\begin{aligned}& \int_0^1 \eta\left[\frac{1}{\eta}\frac{d}{d\eta}\left(\eta\frac{dx^T}{d\eta}\right)(\boldsymbol{P}_\eta^{-1})^T \boldsymbol{W}y + x^T \boldsymbol{R}^T \boldsymbol{W}y\right]d\eta \\ & \quad - \int_0^1 \eta\left[x^T \boldsymbol{W}\boldsymbol{P}_\eta\frac{1}{\eta}\frac{d}{d\eta}\left(\eta\frac{dy}{d\eta}\right) + x^T \boldsymbol{W}\boldsymbol{R}y\right]d\eta = 0\end{aligned} \tag{27}$$

and, on integration by parts, find it reduces to

$$\begin{aligned}& x^T[\boldsymbol{W}\boldsymbol{K}_{\text{rev}} - \boldsymbol{K}_{\text{rev}}^T \boldsymbol{W}]y\bigg|_{\eta=1} \\ & \quad - \int_0^1 \eta x^T[\boldsymbol{W}\boldsymbol{R}_{\text{rev}} - \boldsymbol{R}_{\text{rev}}^T \boldsymbol{W}]y\, d\eta = 0\end{aligned} \tag{28}$$

where we have noted that terms containing the diagonal, irreversible reaction rate matrices $\boldsymbol{R}_{\text{irr}}$ and $\boldsymbol{K}_{\text{irr}}$ fall away by simple cancellation.

We now observe that, for Eq. 28 to be consistent for all x and y in the domain of $\boldsymbol{L}$, we require the expressions

$$k_{ij}w_i = k_{ji}w_j \tag{29}$$

and

$$r_{ij}w_i = r_{ji}w_j \tag{30}$$

to be satisfied simultaneously for all i and j. Here, the w_i are the diagonal components of the matrix $\boldsymbol{W}$. By extending the arguments advanced by Ramkrishna and Amundson (1973) we can show that these conditions are automatically met if the w_i are selected such that

$$w_i = 1/c_i^* \tag{31}$$

where $\boldsymbol{c}^*$ is the equilibrium concentration vector, which, in the absence of irreversible reactions, will satisfy the equation

$$(\boldsymbol{R}_{rev} + \gamma \boldsymbol{K}_{\text{rev}})\boldsymbol{c}^* = \boldsymbol{0} \tag{32}$$

where γ is the surface area to volume ratio for the reactor. This equation has only one independent solution, since $(\boldsymbol{R}_{\text{rev}} + \gamma \boldsymbol{K}_{\text{rev}})$ has rank $(N - 1)$. [Note, however, that $\boldsymbol{R}_{\text{rev}}$ and $\boldsymbol{K}_{\text{rev}}$ can, individually, have lower rank than $(N - 1)$.]

It follows from the principle of microscopic reversibility that

$$(r_{ij} + \gamma k_{ij})c_j^* = (r_{ji} + \gamma k_{ji})c_i^*$$

or

$$(r_{ij} + \gamma k_{ij})1/c_i^* = (r_{ji} + \gamma k_{ji})1/c_j^* \tag{33}$$

Now, if $r_{ij} = r_{ji} = 0$, Eq. 29 is automatically satisfied, and Eq. 30 is trivially so. Similarly, Eqs. 29 and 30 are also satisfied if $k_{ij} = k_{ji} = 0$. The remaining case to be considered is when r_{ij}, r_{ji}, k_{ij} and k_{ji} are all nonzero. Under such conditions we must have

$$\frac{r_{ij}}{r_{ji}} = \frac{k_{ij}}{k_{ji}} \tag{34}$$

since, although the catalyst can change the *rate* of the reaction $A_i \rightleftarrows A_j$, it cannot alter the thermodynamic equilibrium point of this reaction. Equation 33 is

$$r_{ij}\left(1 + \gamma \frac{k_{ij}}{r_{ij}}\right) 1/c_i^* = r_{ji}\left(1 + \gamma \frac{k_{ji}}{r_{ji}}\right) 1/c_j^* \tag{35}$$

which reduces to Eq. 30 when the equality (Eq. 34) is used. In an identical manner, it can be shown that Eq. 33 is also equivalent to Eq. 29, and this completes the proof of out assertion that Eqs. 29 and 30 are automatically satisfied if the w_i are selected in accordance with Eq. 31.

With these results, it is evident that for the operator $\boldsymbol{L}$ to be self-adjoint under the inner product (Eq. 25), the weighting matrix $\boldsymbol{W}$ must be given by

$$\boldsymbol{W} = \operatorname{diag}(1/c_1^*, \ldots, 1/c_N^*) \tag{36}$$

IDENTIFICATION OF θ_m

Sankarasubramanian and Gill (1973, 1974) experienced a number of difficulties in extending their analysis for passive solutes to include heterogeneous wall reactions, difficulties which can be traced directly to the transverse averaging procedure employed, as has been pointed out by DeGance and Johns (1978). It has not been recognized, however, that the transverse averaging used to construct the dispersion coefficients need not be the same as that employed in the definition of the average concentration, θ_m. Indeed, provided the $\boldsymbol{\phi}_k$ used in the expansion (Eq. 13) are determined such that they are consistent with the definition of θ_m, there appears to be no reason why we should restrict θ_m to be the area-average concentration, as has been done in the past. It would seem more appropriate to select θ_m in such a manner as to facilitate the identification of the coefficients $\boldsymbol{\phi}_k$, and thereby avoid the difficulties encountered by Sankarasubramanian and Gill (1973, 1974) while still retaining the coherence of their basic formalism. Here we develop an averaging procedure which enables the identification of the most suitable form, from a computational point of view, for θ_m. The development is an extension of the concept of a "preferred average" first suggested by De Gance and Johns (1978) in their study on single-solute diffusion-reaction problems.

Let λ_0^2 be the smallest eigenvalue, and $\boldsymbol{X}_0$ be the corresponding eigenfunction, of the operator $\boldsymbol{L}$. Then, on multiplying Eq. 8 through by $2\eta \boldsymbol{X}_0^T \boldsymbol{W}$ and integrating over η from 0 to 1, we get

$$\frac{\partial}{\partial \tau} \langle \boldsymbol{X}_0^T \boldsymbol{W} \boldsymbol{\epsilon} \boldsymbol{c} \rangle + \frac{\partial}{\partial \zeta} \langle \boldsymbol{X}_0^T \boldsymbol{W} \boldsymbol{V} \boldsymbol{c} \rangle - \frac{\partial^2}{\partial \zeta^2} \langle \boldsymbol{X}_0^T \boldsymbol{W} \boldsymbol{P}_\zeta^{-1} \boldsymbol{c} \rangle - \langle \boldsymbol{X}_0^T \boldsymbol{W} \boldsymbol{R} \boldsymbol{c} \rangle - 2 \int_0^1 \boldsymbol{X}_0^T \boldsymbol{W} \boldsymbol{P}_\eta^{-1} \frac{\partial}{\partial \eta}\left(\eta \frac{\partial \boldsymbol{c}}{\partial \eta}\right) d\eta = 0 \tag{37}$$

But

$$\begin{aligned} 2 \int_0^1 \boldsymbol{X}_0^T \boldsymbol{W} \boldsymbol{P}_\eta^{-1} \frac{\partial}{\partial \eta}\left(\eta \frac{\partial \boldsymbol{c}}{\partial \eta}\right) \mathrm{d}\eta &= 2 \left[\eta \boldsymbol{X}_0^T \boldsymbol{W} \boldsymbol{P}_\eta^{-1} \frac{\partial \boldsymbol{c}}{\partial \eta} - \eta \frac{d \boldsymbol{X}_0^T}{d\eta} \boldsymbol{W} \boldsymbol{P}_\eta^{-1} \boldsymbol{c}\right]_0^1 + 2 \int_0^1 \frac{d}{d\eta}\left(\eta \frac{d}{d\eta} \boldsymbol{X}_0^T\right) \boldsymbol{W} \boldsymbol{P}_\eta^{-1} \boldsymbol{c}\, d\eta \\ &= -2 \left[\eta \boldsymbol{X}_0^T \boldsymbol{W} \boldsymbol{K} \boldsymbol{c} - \eta \boldsymbol{X}_0^T \boldsymbol{K}^T \boldsymbol{W} \boldsymbol{c}\right]_0^1 - \langle \boldsymbol{X}_0^T \boldsymbol{R}^T \boldsymbol{W} \boldsymbol{c} \rangle - \lambda_0^2 \langle \boldsymbol{X}_0^T \boldsymbol{\epsilon} \boldsymbol{W} \boldsymbol{c} \rangle \end{aligned}$$

and thus

$$\frac{\partial}{\partial \tau} \langle \boldsymbol{X}_0^T \boldsymbol{W} \boldsymbol{\epsilon} \boldsymbol{c} \rangle + \frac{\partial}{\partial \zeta} \langle \boldsymbol{X}_0^T \boldsymbol{W} \boldsymbol{V} \boldsymbol{c} \rangle - \frac{\partial^2}{\partial \zeta^2} \langle \boldsymbol{X}_0^T \boldsymbol{W} \boldsymbol{P}_\zeta^{-1} \boldsymbol{c} \rangle + \lambda_0^2 \langle \boldsymbol{X}_0^{\mathrm{T}} \boldsymbol{\epsilon} \boldsymbol{W} \boldsymbol{c} \rangle - \langle \boldsymbol{X}_0^T (\boldsymbol{W} \boldsymbol{R} - \boldsymbol{R}^T \boldsymbol{W}) \boldsymbol{c} \rangle + 2[\boldsymbol{X}_0^T (\boldsymbol{W} \boldsymbol{K} - \boldsymbol{K}^T \boldsymbol{W}) \boldsymbol{c}]_{\eta=1} = 0 \tag{38}$$

The last two terms are zero because of the nature of the matrices $\boldsymbol{W}$, $\boldsymbol{R}$ and $\boldsymbol{K}$, and hence, if we define the average concentration θ_m by

$$\theta_m = \langle \boldsymbol{X}_0^{\mathrm{T}} \boldsymbol{\epsilon} \boldsymbol{W} \boldsymbol{c} \rangle \equiv \langle \boldsymbol{X}_0, \boldsymbol{c} \rangle \tag{39}$$

we have

$$\frac{\partial \theta_m}{\partial \tau} + \lambda_0^2 \theta_m = -\frac{\partial}{\partial \zeta} \langle \boldsymbol{X}_0^{\mathrm{T}} \boldsymbol{W} \boldsymbol{V} \boldsymbol{c} \rangle + \frac{\partial^2}{\partial \zeta^2} \langle \boldsymbol{X}_0^T \boldsymbol{W} \boldsymbol{P}_\zeta^{-1} \boldsymbol{c} \rangle \tag{40}$$

With this definition of θ_m, we shall see that the equations for the $\boldsymbol{\phi}_k$ are particularly simple—if any other definition is used, the problems encountered by Gill and Sankarasubramanian will again arise, greatly complicating the complete solution to the problem.

DIFFERENTIAL EQUATIONS FOR THE ϕ_k

If we substitute Eq. 13 in Eq. 8, we get

$$\sum_{k=0}^{\infty} \left\{ \boldsymbol{\epsilon} \left[\frac{\partial \boldsymbol{\phi}_k}{\partial \tau} \frac{\partial^k \theta_m}{\partial \zeta^k} + \boldsymbol{\phi}_k \frac{\partial^k}{\partial \zeta^k}\left(\frac{\partial \theta_m}{\partial \tau}\right) \right] + \boldsymbol{V} \boldsymbol{\phi}_k \frac{\partial^{k+1} \theta_m}{\partial \zeta^{k+1}} - \boldsymbol{P}_\zeta^{-1} \boldsymbol{\phi}_k \frac{\partial^{k+2} \theta_m}{\partial \zeta^{k+2}} - \boldsymbol{P}_\eta^{-1} \frac{1}{\eta} \frac{\partial}{\partial \eta}\left(\eta \frac{\partial \boldsymbol{\phi}_k}{\partial \eta}\right) \frac{\partial^k \theta_m}{\partial \zeta^k} - \boldsymbol{R} \boldsymbol{\phi}_k \frac{\partial^k \theta_m}{\partial \zeta^k} \right\} = 0 \tag{41}$$

But, $\partial \theta_m / \partial \tau$ is given by Eq. 40. Thus, after some rearrangement Eq. 41 becomes

$$\sum_{k=0}^{\infty} \left\{ \boldsymbol{\epsilon} \left[\frac{\partial \boldsymbol{\phi}_k}{\partial \tau} - \lambda_0^2 \boldsymbol{\phi}_k - \sum_{j=0}^{k-1} \boldsymbol{\phi}_j \langle \boldsymbol{X}_0^T \boldsymbol{W} \boldsymbol{V} \boldsymbol{\phi}_{k-j-1} \rangle + \sum_{j=0}^{k-2} \boldsymbol{\phi}_j \langle \boldsymbol{X}_0^T \boldsymbol{W} \boldsymbol{P}_\zeta^{-1} \boldsymbol{\phi}_{k-j-2} \rangle \right] + \boldsymbol{V} \boldsymbol{\phi}_{k-1} - \boldsymbol{P}_\zeta^{-1} \boldsymbol{\phi}_{k-2} - \boldsymbol{P}_\eta^{-1} \frac{1}{\eta} \frac{\partial}{\partial \eta}\left(\eta \frac{\partial \boldsymbol{\phi}_k}{\partial \eta}\right) - \boldsymbol{R} \boldsymbol{\phi}_k \right\} \frac{\partial^k \theta_m}{\partial \zeta^k} = 0 \tag{42}$$

The coefficient of each $\partial^k \theta_m / \partial \zeta^k$ can now be set to zero, giving

$$\boldsymbol{\epsilon} \frac{\partial \boldsymbol{\phi}_k}{\partial \tau} - \boldsymbol{P}_\eta^{-1} \frac{1}{\eta} \frac{\partial}{\partial \eta}\left(\eta \frac{\partial \boldsymbol{\phi}_k}{\partial \eta}\right) - (\boldsymbol{R} + \lambda_0^2 \boldsymbol{\epsilon}) \boldsymbol{\phi}_k = \boldsymbol{\mathcal{R}}_k \tag{43}$$

with

$$\boldsymbol{\mathcal{R}}_k = -\boldsymbol{V} \boldsymbol{\phi}_{k-1} + \boldsymbol{P}_\zeta^{-1} \boldsymbol{\phi}_{k-2} + \boldsymbol{\epsilon} \left\{ \sum_{j=0}^{k-1} \boldsymbol{\phi}_j \langle \boldsymbol{X}_0^T \boldsymbol{W} \boldsymbol{V} \boldsymbol{\phi}_{k-j-1} \rangle - \sum_{j=0}^{k-2} \boldsymbol{\phi}_j \langle \boldsymbol{X}_0^T \boldsymbol{W} \boldsymbol{P}_\zeta^{-1} \boldsymbol{\phi}_{k-j-2} \rangle \right\} \tag{44}$$

The boundary conditions on the ϕ_k are

$$\boldsymbol{P}_\eta^{-1}\frac{\partial \phi_k}{\partial \eta} + \boldsymbol{K}\phi_k = 0 \qquad \text{at } \eta = 1 \tag{45}$$

$$\frac{\partial \phi_k}{\partial \eta} = 0 \qquad \text{at } \eta = 0 \tag{46}$$

For consistency, we restrict our initial conditions on c to those which are separable functions of η and ζ. The initial concentration must then be of the form

$$c_0 = h(\eta)Z(\zeta) \tag{47}$$

Hence

$$\theta_{m0} = \langle \boldsymbol{X}_0, c_0\rangle = \langle \boldsymbol{X}_0, h\rangle Z \tag{48}$$

and Eq. 13 is, for $\tau = 0$,

$$c_0 = \sum_{k=0}^{\infty} \phi_{k0}(\eta)\langle \boldsymbol{X}_0, h\rangle \frac{d^kZ}{d\zeta^k}$$

where $\phi_{k0}(\eta)$ is the initial distribution for ϕ_k.

On comparing Eqs. 47 and 48, we find that the initial condition on ϕ_k must be

$$\text{at } \tau = 0 \qquad \phi_k(\eta) = \frac{h(\eta)}{\langle \boldsymbol{X}_0, h\rangle}\delta_{0k} \tag{50}$$

It is also evident, on inspection of the identity

$$\theta_m = \langle \boldsymbol{X}_0, c\rangle = \langle \boldsymbol{X}_0, \phi_0\rangle\theta_m + \sum_{k=1}^{\infty}\langle \boldsymbol{X}_0, \phi_k\rangle \frac{\partial^k\theta_m}{\partial\zeta^k} \tag{51}$$

that the ϕ_k should satisfy

$$\langle \boldsymbol{X}_0, \phi_k\rangle = \delta_{0k} \tag{52}$$

Solutions for the ϕ_k can be constructed using the normalized eigenfunctions of the operator (Eqs. 23–24); the identification of these eigenfunctions follows in the next section.

EIGENFUNCTIONS OF THE OPERATOR L

If $\boldsymbol{X}_n$ is an eigenfunction of the eigenproblem (Eqs. 23–24), we have

$$\boldsymbol{P}_\eta^{-1}\frac{1}{\eta}\frac{d}{d\eta}\left(\eta\frac{d}{d\eta}\boldsymbol{X}_n\right) + \boldsymbol{R}\boldsymbol{X}_n = -\lambda_n^2\boldsymbol{\epsilon}\boldsymbol{X}_n \tag{53}$$

which has the solution

$$\boldsymbol{X}_n = J_0(\boldsymbol{M}_n\eta)\boldsymbol{A}_n \tag{54}$$

where

$$\boldsymbol{M}_n^2 = \boldsymbol{P}_\eta[\lambda_n^2\boldsymbol{\epsilon} + \boldsymbol{R}] \tag{55}$$

and the term in $Y_0(\boldsymbol{M}_n\eta)$ is omitted because of the symmetry condition at $\eta = 0$. The boundary condition at $\eta = 1$ yields

$$[\boldsymbol{M}_nJ_1(\boldsymbol{M}_n) - \boldsymbol{P}_\eta\boldsymbol{K}J_0(\boldsymbol{M}_n)]\boldsymbol{A}_n = \boldsymbol{0} \tag{56}$$

which system of equations can only be consistent if

$$\det[\boldsymbol{M}_nJ_1(\boldsymbol{M}_n) - \boldsymbol{P}_\eta\boldsymbol{K}J_0(\boldsymbol{M}_n)] = 0 \tag{57}$$

The eigenvalues for this eigenproblem are thus those values of λ_n^2 which satisfy the characteristic equation (Eq. 57). Once these have been determined, the coefficient vectors $\boldsymbol{A}_n$ can be evaluated to within arbitrary constants, which are selected to ensure the orthonormality condition

$$\langle \boldsymbol{X}_m, \boldsymbol{X}_n\rangle = 2\int_0^1 \eta\boldsymbol{X}_m^T\boldsymbol{\epsilon}\boldsymbol{W}\boldsymbol{X}_n d\eta = \delta_{mn} \tag{58}$$

holds.

If there are no heterogeneous wall reactions (i.e., $\boldsymbol{K} = \boldsymbol{0}$, the null matrix), the solutions for the eigenvalues and eigenfunctions become somewhat simpler. The characteristic equation (Eq. 57) reduces to

$$\det[\boldsymbol{M}_nJ_1(\boldsymbol{M}_n)] = \prod_{i=1}^{N}\nu_{ni}J_1(\nu_{ni}) = 0 \tag*{(59)$_*$}$$

where the ν_{ni}^2 are the characteristic values of the matrix $\boldsymbol{M}_n^2$. (Note: An asterisk subscript on the equation number indicates the equation is valid for $\boldsymbol{K} = \boldsymbol{0}$ only.) For a given value of n, there are N values of λ_n^2 which will ensure that the condition (Eq. 59) is satisfied, each corresponding to a different equation in the set

$$\nu_{ni}J_1(\nu_{ni}) = 0 \qquad (i = 1,N) \tag*{(60)$_*$}$$

Thus, if α_n is the nth nonzero root of

$$J_1(\alpha) = 0 \tag*{(61)$_*$}$$

then N equations for λ_n^2 result, and these are $\nu_{ni} = \alpha_n (i = 1,N)$. But, since the ν_{ni} all satisfy the same polynomial equation, *viz.*

$$\det[\boldsymbol{M}_n^2 - \nu_n^2\boldsymbol{I}] = 0, \tag*{(62)$_*$}$$

the characteristic equation for the N values of λ_n^2 follows from this expression by replacing ν_n^2 by α_n^2. Thus, with minor rearrangement, we have that the N eigenvalues $\lambda_{n1}^2, \ldots, \lambda_{nN}^2$ are the roots of polynomial

$$\det[\boldsymbol{\epsilon}^{-1}(\alpha_n^2\boldsymbol{P}_\eta^{-1} - \boldsymbol{R}) - \lambda_n^2\boldsymbol{I}] = 0 \tag*{(63)$_*$}$$

i.e., they are the characteristic values of the matrix $\boldsymbol{\epsilon}^{-1}(\alpha_n^2\boldsymbol{P}_\eta^{-1} - \boldsymbol{R})$.

For each value of λ_{ni}^2 $(i = 1,N)$ there is a corresponding eigenfunction $\boldsymbol{X}_{ni}$, which is of the form

$$\boldsymbol{X}_{ni}(\eta) = J_0(\alpha_n\eta)\boldsymbol{A}_{ni} \qquad (i = 1,N) \tag*{(64)$_*$}$$

The coefficients $\boldsymbol{A}_{ni}$ are the characteristic vectors of the matrix $\boldsymbol{\epsilon}^{-1}(\alpha_n^2\boldsymbol{P}_\eta^{-1} - \boldsymbol{R})$, satisfying the equations

$$[\alpha_n^2\boldsymbol{P}_\eta^{-1} - (\boldsymbol{R} + \lambda_{ni}^2\boldsymbol{\epsilon})]\boldsymbol{A}_{ni} = 0 \qquad (i = 1,N) \tag*{(65)$_*$}$$

and should be scaled to ensure normality of the $\boldsymbol{X}_{ni}$, i.e., to ensure

$$\langle \boldsymbol{X}_{ni}, \boldsymbol{X}_{ni}\rangle = 1 \tag*{(66)$_*$}$$

A compact representation of the eigenvalue problem can be obtained when $\boldsymbol{K} = \boldsymbol{0}$ if we define the matrices

$$\overline{\boldsymbol{X}}_n = [\boldsymbol{X}_{n1}, \ldots, \boldsymbol{X}_{nN}] = J_0(\alpha_n\eta)[\boldsymbol{A}_{n1}, \ldots, \boldsymbol{A}_{nN}] = J_0(\alpha_n\eta)\overline{\boldsymbol{A}}_n \tag*{(67)$_*$}$$

and

$$\boldsymbol{\Lambda}_n^2 = \text{diag}(\lambda_{n1}^2, \ldots, \lambda_{nN}^2) \tag*{(68)$_*$}$$

Then $\boldsymbol{X}_n$ satisfies

$$\boldsymbol{P}_\eta^{-1}\frac{1}{\eta}\frac{d}{d\eta}\left(\eta\frac{d}{d\eta}\overline{\boldsymbol{X}}_n\right) + \boldsymbol{R}\overline{\boldsymbol{X}}_n = -\boldsymbol{\epsilon}^{-1}\overline{\boldsymbol{X}}_n\boldsymbol{\Lambda}_n^2 \tag*{(69)$_*$}$$

$$\frac{d}{d\eta}\overline{\boldsymbol{X}}_n = 0 \qquad \text{at } \eta = 0 \qquad \text{and } \eta = 1 \tag*{(70)$_*$}$$

and the orthonormality relation is

$$\langle \overline{\boldsymbol{X}}_m, \overline{\boldsymbol{X}}_n\rangle = 2\int_0^1 \eta\overline{\boldsymbol{X}}_m^T\boldsymbol{\epsilon}\boldsymbol{W}\overline{\boldsymbol{X}}_n d\eta = \delta_{mn}\boldsymbol{I} \tag*{(71)$_*$}$$

SOLUTIONS FOR THE ϕ_k

The expansion of ϕ_k in terms of the eigenfunctions of the operator $\boldsymbol{L}$ is of the form

$$\phi_k = \sum_{n=0}^{\infty}\boldsymbol{X}_n(\eta)T_{nk}(\tau) \tag{72}$$

which, on substitution in Eq. 43, yields

$$\sum_{n=0}^{\infty}\left\{\epsilon \boldsymbol{X}_n \frac{dT_{nk}}{d\tau} - \left[\boldsymbol{P}_\eta^{-1}\frac{1}{\eta}\frac{d}{d\eta}\left(\eta\frac{d}{d\eta}\boldsymbol{X}_n\right) + (\boldsymbol{R} + \lambda_0^2\epsilon)\boldsymbol{X}_n\right] T_{nk}\right\} = \mathcal{R}_k \quad (73)$$

or with Eq. 53,

$$\sum_{n=0}^{\infty}\epsilon \boldsymbol{X}_n\left\{\frac{dT_{nk}}{d\tau} + (\lambda_n^2 - \lambda_0^2)T_{nk}\right\} = \mathcal{R}_k \quad (74)$$

If we now multiply through by $2\eta \boldsymbol{X}_m^T \boldsymbol{W}$, and integrate over η from 0 to 1, taking note of the orthonormality condition (Eq. 58), we find

$$\frac{dT_{mk}}{d\tau} + (\lambda_m^2 - \lambda_0^2)T_{nk} = \langle \boldsymbol{X}_m, \epsilon^{-1}\mathcal{R}_k\rangle \quad (75)$$

The solution to Eq. 75 is

$$T_{mk}(\tau) = e^{-(\lambda_m^2-\lambda_0^2)\tau}\left\{T_{mk}(0) + \int_0^\tau e^{(\lambda_m^2-\lambda_0^2)\tau}\langle \boldsymbol{X}_m, \epsilon^{-1}\mathcal{R}_k\rangle d\tau\right\} \quad (76)$$

The initial conditions (Eq. 50) on the $\boldsymbol{\phi}_k$ can now be invoked to determine the constants $T_{mk}(0)$:

$$T_{mk}(0) = \frac{\langle \boldsymbol{X}_m, \boldsymbol{h}\rangle}{\langle \boldsymbol{X}_0, \boldsymbol{h}\rangle}\delta_{0k} \quad (77)$$

This completes the formal solution for the $\boldsymbol{\phi}_k$, which can now be used in the evaluation of the required dispersion parameters. Explicit representations of T_{m0}, T_{m1} and T_{m2} are given in the Appendix. Before going on to a discussion of our mathematical development, we should note that for $\boldsymbol{K} = \boldsymbol{0}$ we can obtain a more compact result, this time by expanding $\boldsymbol{\phi}_k$ as

$$\boldsymbol{\phi}_k = \sum_{n=0}^{\infty} J_0(\alpha_n \eta)\overline{\boldsymbol{A}}_n \boldsymbol{T}_{nk}(\tau) \quad (78)_*$$

The differential equation for the $\boldsymbol{T}_{nk}(\tau)$ is now

$$\frac{d\boldsymbol{T}_{nk}}{d\tau} + (\boldsymbol{\Lambda}_n^2 - \lambda_{01}^2\boldsymbol{I})\boldsymbol{T}_{nk} = \langle \overline{\boldsymbol{X}}_n, \epsilon^{-1}\mathcal{R}_k\rangle \quad (79)_*$$

with solution

$$\boldsymbol{T}_{nk}(\tau) = e^{-(\Lambda_n^2-\lambda_{01}^2\boldsymbol{I})\tau}\left\{\frac{\langle \overline{\boldsymbol{X}}_n, \boldsymbol{h}\rangle}{\langle \boldsymbol{X}_0, \boldsymbol{h}\rangle}\delta_{0k} + \int_0^\tau e^{(\Lambda_n^2-\lambda_{01}^2\boldsymbol{I})\tau}\langle \overline{\boldsymbol{X}}_n, \epsilon^{-1}\mathcal{R}_k\rangle d\tau\right\} \quad (80)_*$$

where $\boldsymbol{X}_0$ is the vector corresponding to λ_{01}^2.

DISCUSSION

Through an extension of the generalized dispersion theory of Gill and Sankarasubramanian (1970, 1971), we have been able to determine the structure of the convective dispersion parameters appearing in the traditional axial dispersion model commonly employed in the description of mixing and mass transfer in multiphase contactors. With this information on hand, we are now in a position to evaluate critically the general applicability of existing mathematical descriptions of such contactors, and here we make some qualitative observations. A numerical study is given in a companion paper (Hatton and Lightfoot, 1984).

Because of the time dependence of the expansion coefficients $\boldsymbol{\phi}_0$, $\boldsymbol{\phi}_1$ and $\boldsymbol{\phi}_2$, it is clear that the model parameters P, V and R, too, must vary in a time-dependent fashion, and this is at variance with the usual constant-coefficient approximation made in modelling these contactors. This transient behaviour is, of course, well-known for single solute studies (Gill and Sankarasubramanian, 1970, 1971; DeGance and Johns, 1978) where it has been shown that eventually these parameters attain constant asymptotic values, the length of the transient period being dependent on the lateral diffusion rate and system dimensions. For multiphase systems, however, it would seem that the phase interactions arising through interfacial mass transfer can also play a major role in determining this transient behaviour, as can the chemical activity of the species considered. That this is so for non-reactive solutes has been demonstrated elsewhere (Hatton and Lightfoot, 1982), and the magnitudes of the predicted effects under reactive conditions are considered in Part II.

Other significant differences between the usual axial dispersion model and that developed in this work are brought to light when the nondiagonal nature of the matrices Υ_0, Υ_1 and Υ_2 is recognized. It is common practice to assume that the equations for the individual species are coupled only through the mass transfer or reaction terms. Our analysis indicates, however, that the velocity and dispersion coefficient matrices V and P^{-1}, respectively, are nondiagonal, and hence that there is also a coupling of the individual species equations through the spatial derivative terms. These additional species interactions have previously been noted for multisolute problems with heterogeneous, wall-catalyzed reactions (DeGance and Johns, 1980). Here, however, further complications occur as a result of the different averaging policies adopted for the individual phases. This can be an important consideration in the design and analysis of multiphase contactors, since it is usually the flow average concentration of each species that is of primary concern, and the velocity distributions can vary from one phase to the next. Again, we refer to our companion paper (Hatton and Lightfoot, 1984) for an assessment of the importance of these effects.

In anticipation of our numerical results, we can conclude that the dispersion parameters estimated using the constant coefficient model for the analysis of tracer response curves are, for the most part, largely irrelevant for application in the design of multiphase contactors. Furthermore, because of their explicit dependence on the mass transfer and reaction rate constants, even if the transient characters of these parameters were to be correctly accounted for during intraphase dispersion studies, the parameters could not be applied with confidence in the design of systems with interphase mass transfer and chemical reactions.

NOTATION

$\underline{\boldsymbol{A}}_n$ = coefficient vector for $\underline{\boldsymbol{X}}_n$
$\overline{\boldsymbol{A}}_n$ = coefficient matrix for $\overline{\boldsymbol{X}}_n$
$\boldsymbol{c}$ = solute concentration vector
$\boldsymbol{c}^*$ = equilibrium concentration vector
$\boldsymbol{D}_j$ = matrix of eddy dispersion coefficients (j-component)
$\boldsymbol{\mathcal{D}}$ = matrix of molecular diffusion coefficients
$\boldsymbol{h}$ = vector of radial components of initial solute concentration distribution
$\boldsymbol{I}$ = identity matrix
J_ν = Bessel function of the first kind of order ν
$\boldsymbol{K}$ = matrix of reaction rate constants for heterogeneous reactions, $\boldsymbol{K} = \boldsymbol{K}_{\text{rev}} + \boldsymbol{K}_{\text{irr}}$
$\boldsymbol{K}_{\text{irr}}$ = matrix of reaction rate constants for irreversible heterogeneous reactions
$\boldsymbol{K}_{\text{rev}}$ = matrix of reaction rate constants for reversible heterogeneous reactions
k_{ij} = components of matrix $\boldsymbol{K}_{\text{rev}}$
$\boldsymbol{L}$ = matrix operator defined by Eq. 23
$\boldsymbol{M}_n^2$ = matrix defined by Eq. 55
N = total number of species
P = matrix of Peclet numbers for overall axial dispersion (Eq. 22)
$\boldsymbol{P}_j$ = matrix of j-component Peclet numbers, $u_r R_c \boldsymbol{D}_j^{-1}$
R = matrix of effective rate constants (Eq. 20)
$\boldsymbol{R}$ = matrix of reaction rate constants for homogeneous reactions, $\boldsymbol{R} = \boldsymbol{R}_{\text{rev}} + \boldsymbol{R}_{\text{irr}}$
$\boldsymbol{R}_{\text{irr}}$ = matrix of reaction rate constants for irreversible homogeneous reactions
$\boldsymbol{R}_{\text{rev}}$ = matrix of reaction rate constants for reversible homogeneous reactions
R_c = column radius

$\mathcal{R}_k$ = vector defined by Eq. 44
r = radial coordinate
r_{ij} = components of $\boldsymbol{R}_{\text{rev}}$
T_{nk} = time-dependent coefficient in eigenfunction expansion for $\boldsymbol{\phi}_k$ (Eq. 67)
t = time
u_r = reference velocity
$\boldsymbol{V}(r)$ = normalized matrix of velocities, $\boldsymbol{v}(r)/u_r$
$\boldsymbol{V}$ = matrix of effective velocities (Eq. 21)
$v(r)$ = velocity for single-phase, multisolute problem
$\boldsymbol{v}(r)$ = matrix of velocities for multiphase problem
$\boldsymbol{W}$ = matrix of weighting coefficients for inner product (Eq. 25), defined by Eq. 36
w_i = diagonal components of $\boldsymbol{W}$
$\boldsymbol{X}_n$ = eigenfunction of operator $\boldsymbol{L}$
$\bar{\boldsymbol{X}}_n$ = eigenfunction matrix of operator $\boldsymbol{L}$ (for homogeneous reactions only), defined by Eq. 67
Z = axial component of initial solute concentration distribution
z = axial coordinate

Greek Letters

α_n = nth root of $J_1(\alpha) = 0$
γ = surface area to volume ratio for tubular reader
$\boldsymbol{\Delta}$ = matrix defined following Eq. 12
δ_{nm} = Kronecker delta
$\boldsymbol{\epsilon}$ = matrix of hold-up ratios
ζ = normalized axial coordinate z/R_c
η = normalized radial coordinate r/R_c
θ_m = total average concentration, defined by Eq. 39
$\boldsymbol{\Lambda}_n$ = matrix of eigenvalues of $\boldsymbol{L}$ corresponding to α_n (homogeneous reactions only), defined by Eq. 68
λ_n^2 = eigenvalue of operator $\boldsymbol{L}$
ν_{ni}^2 = characteristic value of matrix $\boldsymbol{M}_n^2$
τ = dimensionless time, tu_r/R_c
$\boldsymbol{\Upsilon}_i$ = matrix defined by equation (17)
$\boldsymbol{\Phi}_k$ = matrix of coefficients in Gill expansion (Eq. 13) 13)
$\boldsymbol{\omega}$ = matrix of weighting functions for concentration averaging

Superscripts

T = transpose of vector or matrix
$'$ = dimensional quantity

Subscripts

m = weighted average
r,η = radial component
z,ζ = axial component
0 = initial condition

Other Symbols

$\langle \cdot \rangle$ = area average, $2\int_0^1 \eta(\cdot)d\eta$
$\langle a,b \rangle$ = inner product, $\langle \boldsymbol{a}^T \boldsymbol{\epsilon}\, \boldsymbol{W} \boldsymbol{b} \rangle$
$\{a\}$ = weighted average, $\langle \boldsymbol{\omega a} \rangle$
det = determinant of matrix
diag = diagonal matrix

LITERATURE CITED

Aris, R., "On the dispersion of a solute in a fluid flowing through a tube," *Proc. Roy. Soc.*, **A235**, p. 67 (1956).

Aris, R., "Hierarchies of models in reactive systems," in *Dynamics and Modelling of Reactive Systems*, Eds., W. E. Stewart, W. H. Ray and C. C. Conley, Academic Press, New York (1980).

Astarita, G. A., *Mass Transfer with Chemical Reactions*, Elsevier Publishing Co., Amsterdam, (1967).

Danckwerts, P. V., *Gas-Liquid Reactions*, McGraw-Hill, New York (1970).

DeGance, A. E., and L. E. Johns, "The theory of dispersion of chemically active solutes in a rectilinear flow field," *Appl. Sci. Res.*, **34**, p. 189 (1978).

DeGance, A. E., and L. E. Johns, "On the construction of dispersion approximations to the solutions of the convective diffusion equation," *AIChE J.*, **26**, p. 411 (1980).

Fife, P. C., and K. R. K. Nicholes, "Dispersion in flow through small tubes," *Proc. Roy. Soc.*, **A344**, p. 131 (1975).

Gill, W. N., "Axial dispersion with time variable flow in multiphase system," *AIChE J.*, **15**, p. 745 (1969).

Gill, W. N., "Unsteady tubular reactors-time variable flow and inlet conditions," *Chem. Eng. Sci.*, **30**, p. 1123 (1975).

Gill, W. N., and R. Sankarasubramanian, "Exact analysis of unsteady convective diffusion," *Proc. Roy. Soc.*, **A316**, p. 341 (1970).

Gill, W. N., and R. Sankarasubramanian, "Dispersion of a non-uniform slug in time-dependent flow," *Proc. Roy. Soc.*, **A322**, p. 101 (1971).

Hatton, T. A., "Convective dispersion in multiphase contactors," Ph.D. Thesis, Univ. Wisconsin, Madison (1981).

Hatton, T. A., and E. N. Lightfoot, "On the significance of the dispersion coefficient in two-phase flow," *Chem. Eng. Sci.*, **37**, p. 1289 (1982).

Hatton, T. A., and E. N. Lightfoot, "Dispersion, mass transfer and chemical reaction in multiphase contactors. II: Numerical examples," *AIChE J.* **30**, p. 243 (1984).

Hatton, T. A., and E. T. Woodburn, "Mixing and mass transfer at high liquid rates in the steady state counterflow operation of packed columns," *AIChE J.*, **24**, p. 187 (1978).

Johns, L. E., and A. E. DeGance, "Dispersion approximations to the multicomponent convective diffusion equation for chemically active systems," *Chem. Eng. Sci.*, **30**, p. 1065 (1975).

Linek, V., P. Benes, J. Sinkule, and Z. Krivsky, "Simultaneous determination of mass transfer coefficient and of gas and liquid axial dispersions and hold-ups in a packed absorption column by dynamic response method," *Ind. Eng. Chem. Fund.*, **17**, p. 298 (1978).

Ramkrishna, D., and N. R. Amundson, "Self-adjoint operators from selected nonsymmetric matrices: application to kinetics and rectification," *Chem. Eng. Sci.*, **28**, p. 601 (1973).

Sankarasubramanian, R., and W. N. Gill, "Unsteady convective diffusion with interphase mass transfer," *Proc. Roy. Soc.*, **A333**, p. 115 (1973).

Sankarasubramanian, R., and W. N. Gill, "Correction of unsteady convective diffusion with interphase mass transfer," *Proc. Roy. Soc.*, **A341**, p. 407 (1974).

Subramanian, R. S., W. N. Gill, and R. A. Marra, "Dispersion models of unsteady tubular reactors," *Can. J. Chem. Eng.*, **52**, 563 (1974).

Manuscript received January 7, 1983; revision received May 5, and accepted May 10, 1983.

APPENDIX: COEFFICIENTS T_{m0}, T_{m1} AND T_{m2}

The coefficients T_{m0}, T_{m1} and T_{m2} appearing in the eigenfunction expansions for $\boldsymbol{\phi}_0$, $\boldsymbol{\phi}_1$ and $\boldsymbol{\phi}_2$ are:

$$T_{m0}(\tau) = C_m e^{-\lambda_m^2 \tau}$$

where

$$c_m = \frac{\langle \boldsymbol{X}_m, \boldsymbol{h} \rangle}{\langle \boldsymbol{X}_0, \boldsymbol{h} \rangle}$$

$$T_{m1}(\tau) = \sum_{n=0}^{\infty} C_n \{u_n C_m F(\lambda_m^2 + \lambda_n^2, \lambda_m^2, \tau) + U_{mn} F(\lambda_n^2, \lambda_m^2, \tau)\}$$

where

$$u_n = \langle \boldsymbol{X}_n^T \boldsymbol{W V X}_0 \rangle$$
$$U_{mn} = \langle \boldsymbol{X}_m^T \boldsymbol{W V X}_n \rangle$$

and

$$F(a,b,\tau) = \begin{cases} \dfrac{1}{(a-b)}(e^{-b\tau} - e^{-a\tau}) & (a \neq b) \\ \tau e^{-a\tau} & (a = b) \end{cases}$$

$$\begin{aligned} T_{m2}(\tau) = \sum_{k=0}^{\infty}\sum_{n=0}^{\infty} C_n\{u_k C_m[u_n C_k G(\lambda_m^2,\lambda_m^2 + \lambda_k^2,\lambda_m^2 + \lambda_k^2 \\ + \lambda_n^2,\tau) - U_{kn}G(\lambda_m^2,\lambda_m^2 + \lambda_k^2,\lambda_m^2 + \lambda_n^2,\tau)] \\ + u_k C_k[u_n C_m G(\lambda_k^2,\lambda_m^2,\lambda_m^2 + \lambda_n^2,\tau) \\ - U_{mn}G(\lambda_k^2,\lambda_m^2,\lambda_m^2 + \lambda_n^2,\tau)] \\ - U_{km}[u_n C_k G(\lambda_m^2,\lambda_k^2,\lambda_k^2 + \lambda_n^2,\tau) - U_{kn}G(\lambda_m^2,\lambda_k^2,\lambda_n^2,\tau)]\} \\ + \sum_{n=0}^{\infty} C_n[D_{nm}F(\lambda_k^2,\lambda_m^2,\tau) - d_n C_m F(\lambda_m^2 + \lambda_k^2,\lambda_k^2,\tau)] \end{aligned}$$

where

$$d_n = \langle X_n^T W P_\zeta^{-1} X_0 \rangle$$
$$D_{nm} = \langle X_n^T W P_\zeta^{-1} X_m \rangle$$

and

$$G(a,b,c,\tau) = \frac{1}{(c-b)}\left[\frac{e^{-a\tau} - e^{-b\tau}}{b-a} - \frac{e^{-a\tau} - e^{-c\tau}}{c-a}\right]$$

which has the following limiting forms when two or more of the parameters a, b and c are equal:

(i) $a = b, a \neq c$

$$G(a,a,c,\tau) = \frac{1}{(c-a)}\left[\tau e^{-a\tau} - \frac{e^{-a\tau} - e^{-c\tau}}{c-a}\right]$$

(ii) $a \neq b, a = c$

$$G(a,b,a,\tau) = \frac{1}{(a-b)}\left[\frac{e^{-a\tau} - e^{-b\tau}}{b-a} - \tau e^{-a\tau}\right]$$

(iii) $b = c, b \neq a$

$$G(a,b,b,\tau) = \frac{1}{(b-a)}\left[\frac{e^{-a\tau} - e^{-b\tau}}{b-a} - \tau e^{-b\tau}\right]$$

(iv) $a = b, a = c$

$$G(a,a,a,\tau) = \tau e^{-a\tau}$$

Dispersion, Mass Transfer and Chemical Reaction in Multiphase Contactors

Part II: Numerical Examples

T. A. HATTON and
E. N. LIGHTFOOT

Department of Chemical Engineering
University of Wisconsin
Madison, WI 53706

A numerical study, based on the theoretical developments of Part I of this series, has demonstrated that the chemical activity of a solute can have a significant effect on the convective dispersion behavior of multiphase reactors, and that the dispersion parameters estimated using inert tracers for the individual phases may not be representative of the parameters that should be used in the design of reactive systems. Moreover, the use of different transverse averaging procedures for the individual phases can give rise to additional interaction effects between the phases which are not accounted for in the traditional axial dispersion models. The predicted differences in dispersion parameter values depending on whether the solute is inert or not, are in qualitative agreement with published experimental results.

SCOPE

Procedures for the rational design of multiphase contactors should allow for the reduction in mass transfer efficiency which invariably accompanies axial dispersion of the phases. However, a unique characterization of the dispersion processes for any given hydrodynamic situation using the axial dispersion model does not appear possible, since it has been shown that the rate of interphase mass transfer can modify the effective dispersion processes to a significant degree (Hatton and Lightfoot, 1982). In Part I, an extension of the generalized dispersion theory of Gill and Sankarasubramanian (1970, 1971) to multiphase, reactive problems suggested that further modifications to the convective dispersion processes can be anticipated if the solute is chemically active. Moreover, the theoretical results indicate that the use of arbitrary transverse-averaging procedures for the individual phases may give rise to off-diagonal terms in the dispersion parameter matrices, thereby introducing additional interaction effects between the phases not normally accounted for in the axial dispersion model. The purpose of this paper is to report on a numerical study of these effects, for selected parameter values, and thus to complete the study initiated in Part I.

CONCLUSIONS AND SIGNIFICANCE

The numerical results presented here confirm that the chemical activity of a solute within a given phase can have a significant effect on the dispersion characteristics of multiphase contactors, and suggest that more attention should be paid to large-scale channelling effects in the design of these contactors. This is anticipated to be particularly important for reactors operating under nonisothermal conditions, or for systems ex-

---

Correspondence concerning this paper should be addressed to T. A. Hatton, Department of Chemical Engineering, M.I.T., Cambridge, MA 02139.