A Computational Model For Predicting and Correlating the Behavior of Fixed-Bed Reactors:

I. Derivation of Model for Nonreactive Systems

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A mathematical model is developed for predicting the mixing characteristics of fixed beds of spheres. The model is based on a two-dimensional network of perfectly stirred tanks. By means of the conventional partial differential equation description of flow in fixed beds, the predictions of the new model are compared with experimentally observed axial and radial mixing characteristics. The introduction of a capacitance effect is shown to enable the model to predict the abnormally low axial Peclet numbers observed in liquid-phase systems in the unsteady state.

The mathematical model developed in the first part of this paper is extended to cover chemical reaction in a cylindrical fixed bed of porous catalyst spheres. The mathematical effect on the model of various controlling rate steps, nonconstant property values, and multiple, non-first-order reactions is discussed. After the general discussion a simplified system is chosen to indicate the practical advantages of the model. A single, first-order, irreversible, exothermic reaction is considered to proceed according to an effectively homogeneous rate expression, which varies exponentially with the inverse of absolute temperature. Both steady state and transient cases are calculated for a reactor, the walls of which are maintained at constant temperature.

The fixed bed forms the fluid dynamical environment for many processes of immediate interest to the chemical engineer. Packed reactors and mass exchangers are examples of such processes in which the basic chemical or physical kinetic mechanisms are inseparable from the geometry of the flow system.

Noteworthy experimental and theoretical progress has been made in recent years in elucidating various phenomena which occur in fixed-bed systems. The work of Wilhelm and coworkers (*3, 7*) on the nature of radial mixing in fixed beds is definitive in this particular area. Kramers and Alberda (*6*), McHenry and Wilhelm (*8*), and others (*1, 4, 5*) have investigated the mechanism of axial mixing and proposed models for its description. Voluminous earlier work is available on the evaluation of heat transfer at the tube wall in packed beds and of heat and mass transfer between the packing and the flowing fluid in a bed. Furthermore the factors which influence the course of reactions within a single (catalyst) particle have been the subject of much effective research.

Heretofore no practical mathematical model has been available for combining the environmental and reaction phenomena. The difficulties arising from coupling between material and heat sources in reactive systems were insurmountable, either for purely analytical reasons or because interactions with the environment could not be adequately expressed within the framework of the model.

The purpose of the present work is the development of a mathematical model which is consistent with the available knowledge of mechanistic phenomena. The suitability of the model in terms of available high-speed digital computers for evaluation of solutions is also considered.

The first part of this paper is concerned mainly with evaluating the model as a primary representation of the packed bed environ; nonreactive fluids are thus considered. The model is tested by treating it as if it were an actual physical system and subjecting it to analysis of the type performed previously (*1, 3, 4, 5, 6, 7*). The numerical computations are carried out using an IBM-704 digital computer.

Once the model is established as a predictive as well as a correlative tool it is extended to cover the behavior of reactive systems. The second part of the paper contains an analysis of the mathematical implications of this extension, along with a discussion of the numerical examples. By means of the latter the practical value of the model as a design tool is indicated.

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DEFINITION OF THE PHYSICAL SYSTEM TO BE ANALYZED

In this paper the term "packed bed" is restricted to mean a cylindrical vessel randomly packed with uniform spheres. Cylinder-to-sphere diameter ratio is assumed to be greater than 10. The fluid which flows among the packing is referred to as the *external field* to differentiate it from the immobile fluid phase which may exist in the pore space of the packing. In part I of this paper the packing is taken to be nonporous. The external field is assumed to be a pseudobinary mixture of unreactive components. A material balance is written for only one of these, designated the *tracer component.*

The discussion to follow applies to an external field which is in developed turbulent flow, at least insofar as axial and radial mixing is concerned. Work of the authors cited earlier (*3, 7, 8*) indicates that this criterion is satisfied for N'_{Re} greater than 100, where

$$N'_{Re} = \frac{v\rho_f \epsilon d_p}{\mu_f}$$

Since rigorous application of the equations of change to the external field is impossible, some approximate description of the turbulent mixing phenomena must be introduced. This step, along with the necessary simplification of the boundary situation, re-

sults in a formulation which is fundamentally macroscopic: In particular, functional variations over a length equal to packing sphere diameter are assumed to be small. This restriction will limit the discussion of part II to chemical reactions which are not too rapid.

Other assumptions which are understood to apply (unless otherwise stated) are:

1. Molar density and heat capacity of the external field are constant.
2. Molecular-level fluxes are negligible when compared to the equivalent turbulent fluxes.
3. Turbulent mass and thermal diffusivities are equal; that is the mechanism of transport is the same. Thermal conductivity of the packing is negligible.
4. The bed is axially symmetric.

MATHEMATICAL MODELS OF THE EXTERNAL FIELD

In this paper the term "model" refers to a primary mathematical representation of the behavior of the external field, that is a model is intended to be a mathematical tool for the prediction of temperature and/or concentration distributions in the external field. Distinction should be drawn between mathematical models and physical models on which they may be based. The mathematical formulations developed here have as foundations certain physical observations concerning the macroscopic behavior of fixed beds. These foundations are not considered to be restrictive; modifications in the formulations will be made to improve the agreement between prediction and experimental results, although these modifications may not be immediately justifiable from a physical standpoint.

Solutions of model equations under boundary and initial conditions appropriate to given design problems must be physically reasonable and complete. This in turn means that the model must account for all physical as well as chemical factors which are important in the problems.

In a restricted sense a model should require only specification of external conditions and static fluid (and solid) property values to predict the desired variables throughout the external field. This requirement is taken to apply to problems in which boundary conditions vary with time, that is to transient or unsteady state cases.

If it is to be of practical as well as academic interest, a model must be mathematically tractable. Solutions to reasonably complex problems must be obtainable either analytically or through application of known numerical techniques. Moreover the numerical evaluation of the solutions must be feasible, with available computing machinery used.

THE DIFFERENTIAL BALANCE MODEL

The standard formulation of the external field problem is a set of differential balances derived from the equations of change for a homogeneous fluid. The derivation has been discussed by numerous authors (2) so that only those results necessary for later comparisons are given here. Under the assumptions stated earlier the differential model material balance for the trace component is

$$\frac{1}{N_{Pe_x}}\frac{\partial^2 C}{\partial x^2}+\frac{1}{N_{Pe_r}}\left[\frac{\partial^2 C}{\partial r^2}+\frac{1}{r}\frac{\partial C}{\partial r}\right]-\frac{\partial C}{\partial x}=\frac{\partial C}{\partial t} \quad (1)$$

The complete determination of a system which is described by these differential balances requires the statement of initial and boundary conditions. A compatible form of these is

$$C(x,r,o)=f(x,r) \quad (2)$$

$$C(o,r,t)-\frac{1}{N_{Pe_x}}\frac{\partial C(o,r,t)}{\partial x}=g(r,t) \quad (3)$$

$$\frac{\partial C(N,r,t)}{\partial x}=0 \quad (4)$$

$$\frac{\partial C(x,M,t)}{\partial r}=0 \quad (5)$$

From consideration of Equations (3) and (4) (or the others) it can be seen that determining the tracer concentration is a boundary-value problem in partial differential equations. Similar considerations would apply to a heat-balance equation.

The evaluation of the radial and axial Peclet numbers by application of solutions of Equation (1) to experimental data is fully discussed in the literature (3 to 8). A summary of results for fully developed turbulent flow is given in Table 1.

Except for the case of the liquid N_{Pe_x} the Peclet numbers in Table 1 are practically constant for $N_{Re} > 100$. The results for liquid systems are apparently anomalous. Some additional feature is needed in the differential model to explain the dependence of N_{Pe_x} on both the molecular properties of the liquid system and the experimental technique employed. An explanation in terms of capacity effects has been suggested (4, 5), but its inclusion in the differential-balance model would result in mathematical complications which are incommensurate with the applicability of the model.

THE FINITE ELEMENT BALANCE MODEL

Certain of the shortcomings of the differential-balance model suggest the necessity for an altogether different type of primary representation of the external field. Specifically a model is desired which is not subject to the handicaps characteristic of boundary-value partial differential equations. The alternative developed here is referred to as the *finite element balance or finite stage model.* It is based on the fundamentally heterogeneous nature of the packed bed; sphere diameter becomes the natural measure of length, and the void volume associated with a sphere is taken as the volume element for the balances.

A one-dimensional stage model is suggested by the characteristics of a form of Equation (1). In a gaseous system where radial variation is absent, the differential mass balance is

$$\frac{1}{2}\frac{\partial^2 C}{\partial x^2}-\frac{\partial C}{\partial x}=\frac{\partial C}{\partial t} \quad (N_{Pe_x}=2) \quad (6)$$

Several investigators have reported that solutions of Equation (6) for particular boundary conditions may be approximated by solutions of a system of ordinary differential equations. This equivalent set of equations was pointed out to be the mathematical representation of a number of perfectly stirred tanks arranged in series, where each tank has a mean residence time of (d_p/v). The dimension of the set, that is the number of tanks in series, is the ratio of bed length to sphere diameter. As this ratio increases, the numerical agreement between the solutions given by the two types of equations improves.

The material-balance equation for a trace component in the ith stage of a series of N perfectly stirred stages is given by

$$Q(C_{i-1}-C_i)=V\frac{dC_i}{dt} \quad (7)$$

If V/Q is equated to d_p/v, (7) becomes

$$C_{i-1}-C_i=\frac{dC_i}{dt} \quad (8)$$

The conditions which must be set to complete the specification of the problem are

$$C_i(0)=\overline{f}(i) \qquad 1\leq i\leq N \quad (9)$$

$$C_o(t)=\overline{g}(t) \qquad t>0 \quad (10)$$

The one-dimensional physical model on which (8) is based was predated by a three-dimensional perfect mixer model for turbulent radial mixing. Latinen (7) presented a derivation of theoretical radial mixing in packed beds based on statistical considerations, in which the perfect mixer array was the turbulent flow limiting case. His results provide the

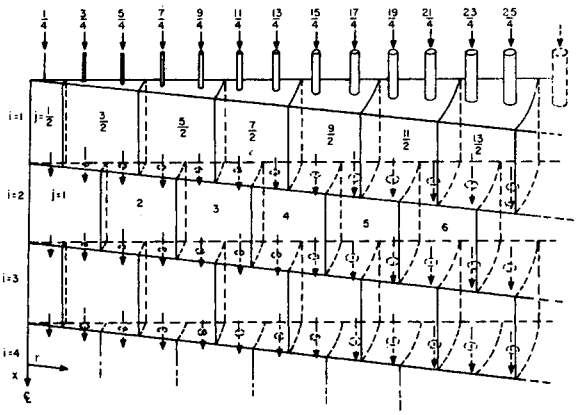

Fig. 1. Schematic representation of the arrangement of stages and the configuration of the flow pattern in the basic stage model.

basis for extending (8) to three dimensions, with the consequent inclusion of the turbulent radial-mixing phenomenon in the mathematical model.

Because of radial symmetry the array of mixed stages may be reduced to two dimensions immediately. A geometrically regular arrangement which is consistent with the statistical model mentioned above is shown in Figure 1. The presence of two possible outlets from each perfectly stirred volume element produces a macroscopic or mixed average equivalent of particulate random flight. Since each stage represents a perfectly stirred tank, the axial-mixing mechanism is retained. The mathematical formulation of this regular array is tested later by means of experimental observations of radial- and axial-mixing data.

In the transition to two dimensions it is assumed that angular flow is absent and that the spatial density of stages (that is void fraction) is independent of position in the bed. Each stage in the two-dimensional network represents the balance-volume elements, or voids, contained in an annular disk, of which only a segment is shown in Figure 1. The stage with indices i, j includes the voids in the region bounded (a) by two planes at distances $(i-1)d_p$ and id_p from the inlet end of the bed, and (b) by two concentric cylinders of radius $K(j-1)d_p$ and Kjd_p. As before $1 \leq i \leq N$, where $N = L/d_p$, assumed integral. The offset arrangement shown in Figure 1 is obtained by letting j take on the values 1/2, 3/2, 5/2, . . . M when i is an odd integer, and the values 1, 2, 3. . . M when i is even. The constant K represents the multiple of half-particle diameters which the fluid side-steps in an actual bed. It is evaluated later. $2M = D/Kd_p$ is also assumed to be an integer, so that either the even or odd rows (but not both) will have fractional stages at the wall.

The total-balance volume of the i, jth stage is given by

$$V_{i,j} = \epsilon A_j d_p \tag{11}$$

From simple geometric considerations

$$A_j = \pi K d_p^2 [j^2 - (j-1)^2]$$
$$= \pi K d_p^2 [2j-1] \tag{12}$$

Thus the stage volume is only a function of the radial index j; that is

$$V_{i,j} = V_j = \epsilon \pi K d_p^3 (2j-1) \tag{13}$$

For the particular case $j = 1/2$, $(j-1) = 0$ by symmetry. That is

$$V_{1/2} = \epsilon \pi K d_p^3 \left(\frac{1}{2}\right)^2 \tag{14}$$

The total volumetric throughput of the i, jth stage is

$$Q_j = A_j \epsilon v \tag{15}$$

and the mean residence time for the stage is

$$\frac{V_j}{Q_j} = \frac{d_p}{v} \tag{16}$$

as desired in the one-dimensional analogy. Thus Equation (8) still applies to a stage in the two-dimensional model if the feed concentration C_{i-1} is understood to be an average of output concentrations from the two stages diagonally behind (or above) the stage i, j. This average is weighted according to the relative magnitudes of the two streams which comprise the throughput Q_j. If these streams are designated Q_{Aj} and Q_{Bj} for the moment, the average concentration $\phi_{i-1,j}$ is defined by

$$\phi_{i-1,j} = \frac{Q_{Aj} C_{i-1,j-1/2} + Q_{Bj} C_{i-1,j+1/2}}{Q_j} \tag{17}$$

Since the velocity is not a function of j, Q_{Aj} and Q_{Bj} can be assigned unique values. From (12) and (15) it follows that

$$Q_j = Q_{Aj} + Q_{Bj} = \epsilon \pi K d_p^2 v [j^2 - (j-1)^2] \tag{18}$$

The areas of overlap of the lateral faces of stages $i-1$, $j-1/2$ and $i-1$, $j+1/2$ on stage i, j determine the ratio of Q_{Aj} to Q_{Bj}; that is

$$\frac{Q_{Aj}}{Q_{Bj}} = \frac{[(j-1/2)^2 - (j-1)^2] \epsilon \pi K d_p^2 v}{[j^2 - (j-1/2)^2] \epsilon \pi K d_p^2 v}$$
$$= \frac{j-3/4}{j-1/4} \tag{19}$$

If (18) and (19) are solved simultaneously for Q_{Aj} and Q_{Bj}, and the results substituted into (17):

$$\phi_{i-1,j} = \frac{(j-3/4)\, C_{i-1,j-1/2} + (j-1/4)\, C_{i-1,j+1/2}}{(2j-1)} \tag{20}$$

Again for the particular case $j = 1/2$ special treatment is necessary. $(j-3/4)$ is set equal to zero and removed from the denominator, resulting in

$$\phi_{i-1,1/2} = C_{i-1,1} \tag{21}$$

At the wall $C_{i-1,M-1/2}$ is equal to the imaginary $C_{i-1,M+1/2}$ by reflection, so that

$$\phi_{i-1,M} = C_{i-1,M-1/2} \tag{22}$$

The reflection property follows from the no-flux boundary condition at the wall.

A heat balance may also be written analogous to the material balance (8). In this case a feed temperature T_{i-1} would appear. Again transition to two dimensions requires only the redefinition of the inlet stream as a mixture of two outputs of the previous stages; the average inlet temperature $\psi_{i-1,j}$ which replaces T_{i-1} can be found by arguments completely parallel to the above. Thus

$$\psi_{i-1,j} = \frac{(j-3/4) T_{i-1,j-1/2} + (j-1/4) T_{i-1,j+1/2}}{(2j-1)} \tag{23}$$

Since the solid packing has heat capacity, a term should appear in the heat balance to account for heat transfer between the solid and the external field. In the present discussion it is assumed that this transfer is fast enough (and that temperature gradients inside the particles are small enough) so that the particle temperature may be considered equal to the fluid temperature. Separate heat and material balances for the packing are considered in the second part of this paper.

The complete finite stage model (for a stage not at the wall) consists therefore of the two equations:

$$\phi_{i-1,j} - C_{i,j} = \frac{dC_{i,j}}{dt} \tag{24}$$

$$\psi_{i-1,j} - T_{i,j} = \beta \frac{dT_{i-j}}{dt} \quad (25)$$

where $\beta = 1 + C_s\rho_s(1-\epsilon)/C_p\rho_F\epsilon$.

For a wall stage (25) must be modified to allow for heat flux through the tube wall. If Newtonian radiation is assumed to apply at the wall surface, (25) may be written

$$\psi_{i-1,M} - T_{i,M} + N_{ST_W}(\overline{T}_{W_i} - T_{i,M}) = \beta \frac{dT_{i,M}}{dt} \quad (26)$$

where N_{ST_W} is defined by

$$N_{ST_W} = \frac{h_W A_{W_i}}{Q_M C_p \rho_F} \quad (27)$$

Since

$$A_{W_i} = 2\pi K M\, d_p^2\, \epsilon \quad (28)$$

and from (12) and (15)

$$Q_M = \pi K d_p^2 \epsilon v\,[2M-1] \quad (29)$$

it follows that

$$N_{ST_W} = \left(\frac{h}{G_M C_p}\right)\cdot\left(\frac{2M}{2M-1}\right) \simeq \frac{h}{G_M C_p} \quad (30)$$

if M >> 1.0. These arguments apply to rows in which the wall stage is not fractional. For the alternate rows (either even or odd i, depending on whether $2M$ is odd or even) the wall stage will have a lateral face area given by

$$A_{M_f} = \pi K d_p^2\,[M^2 - (M-1/2)^2] = \pi K d_p^2\,[M-1/4] \quad (31)$$

so that

$$Q_{M_f} = \pi K d_p^2 \epsilon v\,[M-1/4] \quad (32)$$

However since A_{W_f} is still given by (28)

$$N_{ST_{W_f}} = \left(\frac{h}{G_M C_p}\right)\left(\frac{2M}{M-1/4}\right) \quad (33)$$

Thus $N_{ST_{W_f}} = 2N_{ST_W}$ if $M >> 1$.

If N_{ST_W} (or $N_{ST_{W_f}}$, as the case may be) is assumed constant for a given stage, (26) may be written

$$\psi'_{i-1,M} - T_{i,M} = \beta' \frac{dT_{i,M}}{dt} \quad (34)$$

where

$$\psi'_{i-1,M} = \frac{\psi_{i-1,M} + N_{ST_W}\overline{T}_{W_i}}{1 + N_{ST_W}} \quad (35)$$

$$\beta' = \frac{\beta}{1 + N_{ST_W}} \quad (36)$$

which brings the wall stage heat balance into the same form as the normal stage Equation (25).

It follows from the form of Equations (24) and (25) and from the definitions of $\phi_{i-1,j}$ and $\psi_{i-1,j}$ that the solution of the equations for a particular (i, jth) stage depends only on the initial conditions $C_{i,j}(0)$ and $T_{i,j}(0)$ and on the solutions for stages in the $i-1$th row.

The significance of this fact is that the entire set of stage equations representing the packed bed can be solved as an initial-value problem. That is input functions from the upstream stages are forcing functions rather than boundary conditions. Since a given stage is not affected by events downstream, the calculation of solutions to the complete set of equations may proceed sequentially, beginning at the inlet row of stages. The inlet-stream functions $C_{o,j}(t)$ and $T_{o,j}(t)$ determine $\phi_{o,j}$ and $\psi_{o,j}$ as a function of time. The latter, along with the initial conditions $C_{1,j}(0)$ and $T_{1,j}(0)$, allow solution of (24) and (25) for $C_{1,j}$ and $T_{1,j}$, $j = 1/2, 3/2, \ldots$, for all $t > 0$. These first row solutions determine $\phi_{1,j}$ and $\psi_{1,j}$ which in turn allow calculation of $C_{2,j}$ and $T_{2,j}$, $j = 1, 2, \ldots$, all $t > 0$. This sequence is continued through $i = N$.

The importance of this initial-value character of the stage-model equations can hardly be overstated. In the simple flow problems discussed up to this point the balance equations for a given stage have been linear and independent. Analytical solutions to Equations (24) and (25) are available through application of standard techniques. For the chemical reactor problems to be discussed in part II direct numerical solution is necessitated by nonlinear coupling terms in the balances. Efficient numerical procedures are available for ordinary differential equations, while no such easy path presents itself in the case of nonlinearly coupled partial differential equations.

The relative simplicity of the stage-model formulation is exemplified by the steady state form of (24). If the inlet functions $\phi_{o,j}$, $0 \leq j \leq M$ are time independent, the material balance for the i, jth stage will eventually be given by

$$\phi_{i-1,j} - C_{i,j} = 0 \quad (37)$$

The problem becomes merely a mixed average equivalent of the Galton quincunx with wall effects. The solution is obtainable by trivial algebraic manipulations.

Several of the restrictions assumed may be removed from the stage-model formulation without complicating its structure or disturbing its initial-value nature. First if empirical information concerning gross velocity profiles is available, the model may be modified quite simply to account for radial variation in velocity. When one assumes that the functionality is expressed as

$$v(j) = f^{-1}(j)\, v(0) \quad (38)$$

the dimensionless time can be redefined by

$$\overline{t} = \frac{Q_o}{v_j} t' = \frac{t' v(0)}{d_p} \quad (39)$$

The material-balance Equation (24) becomes then

$$\phi_{i-1,j} - C_{i,j} = f(j) \frac{dC_{i,j}}{d\overline{t}} \quad (40)$$

The heat balance (25) is altered in the same manner.

The assumptions of constant molar density and heat capacity are questionable for gas-phase systems in which large temperature variations occur within the bed. Coefficients which depend on temperature may be added to the heat-balance equation, for example, to eliminate the need for these restrictions. Equation (25) is modified to read

$$\overline{\psi}_{i-1,j} - \sigma(T_{i,j})T_{i,j} = \overline{\beta}(T_{i,j})\frac{dT_{i,j}}{dt} \quad (41)$$

where

$$\overline{\psi}_{i-1,j} = \frac{(j-3/4)\,(C_pT)_{i-1,j-1/2} + (j-1/4)\,(C_pT)_{i-1,j+1/2}}{(2j-1)\,(C_p)_o} \quad (42)$$

$$\sigma(T_{i,j}) = \frac{(C_p)_{i,j}}{(C_p)_o} \quad (43)$$

$$\overline{\beta}(T_{i,j}) = \frac{(C_p\rho_F)_{i,j} + \frac{1-\epsilon}{\epsilon}(C_s\rho_s)_{i,j}}{(C_p\rho_F)_o} \quad (44)$$

The mass velocity is assumed not to depend on radial position.

Since both σ and $\overline{\beta}$ are arbitrary functions of the dependent variable $T_{i,j}$, it is apparent that (41) cannot be solved analytically. However the nature of the variation of these functions with temperature is normally such that their values from one of the stages $i-1$, $j \pm 1/2$ may be used as a good first approximation in the numerical solution. That is the change in temperature over a length of bed corresponding to one stage may be assumed to produce changes in σ and $\overline{\beta}$ which are quite small relative to the magnitudes of σ and $\overline{\beta}$. This characteristic effectively guarantees rapid convergence of simple iterative correction procedures in the process of numerical integration of (41). Similar arguments hold for the solution of the material balance when its coefficients depend on concentration.

The numerical efficiency with which these corrections for minor nonlinearities (and later for major nonlinear

coupling) can be made is due primarily to the sequential nature of the finite-stage model. Where iterative procedures are required, convergence has only to be obtained at one geometric position at a time. In the boundary-value problem represented by the differential-balance model an iteration scheme must be applied simultaneously at all positions in the bed. For given coefficient functionalities the radius of convergence (that is the allowable error in the first approximation in the iterative procedure) is necessarily much smaller for an entire system than for a single point. Furthermore that rate of convergence, and hence the speed of the numerical procedure, must be much slower for a multidimensional field of points, even if the initial guess at all points is good enough for eventual convergence to occur.

THE RELATIONSHIP BETWEEN THE DIFFERENTIAL-BALANCE AND FINITE-STAGE MODELS FOR THE EXTERNAL FIELD

The agreement between solutions to Equation (6) and the set represented by (8) is not fortuitous, nor is it dependent entirely on the intuitive connection between a packed bed and a series of perfectly mixed tanks. Equation (6) may be converted into a differential difference equation by the process of substituting finite difference approximations for the axial derivations only. If lowest order central differences are used, (6) becomes

$$\frac{1}{2(\Delta x)^2}[C_{i-1}-2C_i+C_{i+1}]-\frac{1}{2\Delta x}$$

$$[C_{i+1}-C_{i-1}]+E[0(\Delta x^3)]=\frac{\partial C_i}{\partial t} \quad (45)$$

Ignoring the third-order error term and letting $\Delta x = 1$ one obtains

$$\frac{1}{2}[C_{i-1}-2C_i+C_{i+1}]$$

$$-\frac{1}{2}[C_{i+1}-C_{i-1}]=\frac{dC_i}{dt} \quad (46)$$

The derivative on the right is written as ordinary, since only t is a differential variable at this point. Collecting terms one gets

$$C_{i-1}-C_i=\frac{dC_i}{dt} \quad (47)$$

which is the complete equivalent of (8). When one sets the dimensions, $\Delta x = 1$ is the same as dividing the one-dimensional bed into units of length d_p. The third-order error term becomes less important as the ratio L/d_p increases, so that (47) must approach a true equality as the number of particles in the axial dimension of the bed becomes large. In any case a fundamental requirement of the differential-balance model was that the functional variation over a length of bed equivalent to the sphere diameter should be small. This has the effect of making higher-order terms in the difference approximations negligible.

Table 1. Summary of Consensus Values for Peclet Numbers from the Literature

	N_{Pe_r}	N_{Pe_z}
Gases	10-12	2
Liquids	10-12	0.3-1.0

At some point in the derivation of (47) the transition from a boundary-value problem to one of initial-value nature occurs. The boundary condition at $x = N$ for the one-dimensional case is

$$\frac{\partial C(N,t)}{\partial x}=0 \quad (48)$$

This condition no longer has any effect on the solution of the differential-difference equation set represented by (47). The disappearance of the mathematical feedback which makes (48) necessary can be traced most easily if the differencing process is completed. Removal of the assumptions that $N_{Pe_z} = 2$ and substitution of the first-order backward difference approximation for the time derivative in (45) leads to

$$\frac{1}{N_{Pe_z}(\Delta x)^2}[C_{i-1,\,t}-2C_{i,\,t}+C_{i+1,\,t}]$$

$$-\frac{1}{2\Delta x}[C_{i+1,\,t}-C_{i-1,\,t}]=\frac{C_{i,\,t}-C_{i,\,t-1}}{\Delta t} \quad (49)$$

Equation (49) may be rearranged to give

$$\left[\frac{1}{2}+\frac{N_{Pe_z}\Delta x}{4}\right]C_{i-1,\,t}$$

$$-\left[1+\frac{N_{Pe_z}(\Delta x)^2}{2\Delta t}\right]C_{i,\,t}$$

$$+\left[\frac{1}{2}-\frac{N_{Pe_z}\Delta x}{4}\right]C_{i+1,\,t}$$

$$=-\frac{N_{Pe_z}(\Delta x)^2}{2\Delta t}C_{i,\,t-1} \quad (50)$$

Table 2

$i \downarrow$ \ $j \rightarrow$	1/2	9/2	15/2	Avg.	
20	8.3	7.5	—	—	
30	8.6	7.8	8.2	8.2	
40	8.7	8.0	7.9	8.2	$1 \leq i \leq 70$
50	8.9	8.0	7.8	8.2	$0 < j \leq 19/2$
60	8.9	8.1	7.7	8.2	

Equation (49) may be written in differenced form as

$$C_{N+1,\,t}=f(C_{N,\,t};C_{N-1,\,t};C_{N-2,\,t};\ldots.) \quad (51)$$

where N is the last interior axial grid point. Equation (51) is used to eliminate $C_{N+1,\,t}$ from the corresponding Equation (50) resulting in

$$\left[\frac{1}{2}+\frac{N_{Pe_z}\Delta x}{4}\right]C_{N-1,\,t}$$

$$-\left[1+\frac{N_{Pe_z}(\Delta x)^2}{2\Delta t}\right]C_{N,\,t}$$

$$+\left[\frac{1}{2}-\frac{N_{Pe_z}\Delta x}{4}\right]f$$

$$=-\frac{N_{Pe_z}(\Delta x)^2}{2\Delta t}C_{N,\,t-1} \quad (52)$$

It is apparent from this that the effect of (48) must disappear as $N_{Pe_z}\Delta x/2 \rightarrow 1$. In this limit (50) becomes

$$C_{i-1,\,t}-\left[1+\frac{\Delta x}{\Delta t}\right]C_{i,\,t}$$

$$=-\frac{\Delta x}{\Delta t}C_{i,\,t-1} \quad (53)$$

which is the corresponding differenced form of the equation for a stirred tank only if $\Delta x = 1$ (and consequently $N_{Pe_z} = 2$).

Although the stage model was specifically derived for the turbulent flow region where $N_{Pe_z} = 2$ (for gases), an equivalent set of stage equations can be set up for a system with any characteristic N_{Pe_z}. If t^* is defined as

$$t^*=\frac{N_{Pe_z}}{2}t \quad (54)$$

(53) becomes

$$C_{i-1,\,t}-C_{i,\,t}=\frac{C_{i,\,t}-C_{i,\,t-1}}{\Delta t^*} \quad (55)$$

which does correspond to the finite-stage equation

$$C_{i-1}-C_i=\frac{dC_i}{dt^*} \quad (56)$$

The number of stages equivalent to a bed of length L is now

$$N^*=\frac{L}{d_p\,\Delta x}=\frac{N_{Pe_z}L}{2d_p}=\frac{N_{Pe_L}}{2} \quad (57)$$

SIMULATION OF PHYSICAL EXPERIMENTS ON PACKED BEDS WITH THE FINITE-STAGE MODEL OF THE EXTERNAL FIELD

Two general types of experimental procedure have been reported for evaluating the effective Peclet numbers listed in Table 1. Particular experiments were designed to maximize one component of the turbulent flux vector relative to the other. In most cases the

TABLE 3. EFFECTIVE AXIAL PECLET NUMBERS AS A FUNCTION OF δ AND f_1

$f_1 = 0.8$

$\delta\downarrow$ \ $i\rightarrow$	60	70	80	90
8	1.975	1.976	1.978	1.979
1	1.851	1.853	1.855	1.856
0.125	1.230	1.230	1.230	—
0.09375	—	1.080	—	—
0.0625	—	0.850	—	—
0.03125	—	0.359	—	—

$f_1 = 0.9, i = 70$

δ	0.0625	0.03125	0.015625	0.0078125	0.003906125
N_{Pe_x}	1.52	1.22	0.83	0.49	0.30

differential-balance model was used as a means of analysis; that is the solution of an appropriate form of Equation (2) was used in conjunction with the experimental data to obtain the appropriate Peclet numbers.

The most common technique for measuring N_{Pe_r} involved the introduction of a tracer stream at some point in the bed, usually on the tube axis at or near the beginning of the packed section. At steady state, radial concentration profiles of the tracer were then measured at various axial positions downstream from the point of introduction (3, 7). In this analysis the axial component of the turbulent mixing was shown to be negligible.

Simulation of this particular experimental procedure is readily accomplished by the use of the finite stage model. The steady state concentrations of all stages in an arbitrary network are given by (37) and the definition of $\phi_{i-1,\,j}$. The only external condition required is the stipulation of the tracer source in the inlet stream, which is given by

$$\phi_{0,\,1/2} = q$$

$$\phi_{0,\,3/2} = \phi_{0,\,5/2} = \ldots \phi_{0,M} = 0$$

where q is arbitrary. The algebraic determination of the $C_{i,\,j}$, $1 \leq i \leq N$, $0 < j < M$, results in a two-dimensional set of concentration values which are the stage model equivalent of the experimental data.

This set of concentration values may now be operated upon as if it were a discrete sampling of a continuous function $C(r, x)$. The appropriate form of (1) is used in the analysis so that the stage-model results may be compared directly with the N_{Pe_r} of Table 1. At steady state (1) becomes

$$\frac{1}{2}\frac{\partial^2 C}{\partial x^2} + \frac{1}{N_{Pe_r}}\left[\frac{\partial^2 C}{\partial r^2} + \frac{1}{r}\frac{\partial C}{\partial r}\right]$$

$$-\frac{\partial C}{\partial x} = 0 \qquad (58)$$

if $N_{Pe_x} = 2$. Although (58) could be solved with appropriate boundary conditions and the solution used to obtain N_{Pe_r} at various positions in the model, a more direct approach is available. Solved for N_{Pe_r} (58) is

$$N_{Pe_r} = \frac{\dfrac{\partial^2 C}{\partial r^2} + \dfrac{1}{r}\dfrac{\partial C}{\partial r}}{\dfrac{\partial C}{\partial x} - \dfrac{1}{2}\dfrac{\partial^2 C}{\partial x^2}} \qquad (59)$$

If derivatives appearing here are replaced by finite difference approximations, (59) may be written in symbolic operator form as

$$N_{Pe_r}]_{i,\,j} = P_r\,(\Delta x, \Delta r, j)\; C_{i,\,j} \qquad (60)$$

The exact form of P_r depends on the difference formulas employed.

Table 2 presents the results of such a calculation. The point values of N_{Pe_r} were obtained by application of the P_r operator to a set of stage concentrations calculated on an IBM-704 computer. The system parameters were $N = 70$, $2M = 19$, and $q = 1.0$. The P_r operator included central differences up to the seventh order in both radial and axial directions.

The value of K can now be determined which will bring the model into exact agreement with any given experimental value of N_{Pe_r}. This value is

$$K = \sqrt{\frac{8.2}{N_{Pe_r}}} \qquad (61)$$

The upper limit for the radial subscript j is thus

$$M = \frac{D}{2d_P\sqrt{\dfrac{8.2}{N_{Pe_r}}}} \qquad (62)$$

The majority of reported determinations (4, 5, 6, 8) of axial mixing have involved unsteady state experiments. The use of time-varying tracer concentration in the total inlet stream to a bed was the most common technique. Piston flow was assumed so that the analysis could be based on a one-dimensional model. Solutions of the model equations were applied to output concentration (vs. time) curves, and the results were reported in the form of effective axial Peclet numbers. Probably because of bed-capacitance effects (4), agreement was not obtained between N_{Pe_x} for gases and liquids, even for well-developed turbulent flow.

As represented by (24) and (25) the finite stage model necessarily predicts an axial Peclet number of 2.0. This was seen to be a characteristic of a series of perfectly stirred tanks if V/Q for each tank was set equal to d_p/v. However an intuitive extension of the basic model can enable it to simulate the unsteady state behavior of actual packed beds.

Because of the irregular shape of a void in a packed bed the fluid in some positions is poorly mixed even at large values of N'_{Re}. Near sphere surfaces and in the recesses formed by the tangency of spheres laminar or even quiescent conditions must exist. The effect of this unmixed portion on the stage model could be expressed in a variety of ways. In order to avoid undue mathematical complications a very rough approximation is used here. Each stage is arbitrarily divided into two perfectly mixed parts. The larger is defined to have the same function as the entire stage has in the basic model. The smaller part is merely a capacitance volume; it has no inlet or outlet, except a diffusional surface in common with the larger part of the stage. Consequently each stage now has associated with it two concentration variables. The over-all stage material balance for a tracer becomes

$$\phi_{i-1,\,j} - C_{i,\,j} = f_1\frac{dC_{i,\,j}}{dt} + (1-f_1)\frac{d\overline{C}_{i,\,j}}{dt} \qquad (63)$$

The subsidiary balance on the capacitance part is

$$(1-f_1)\frac{d\overline{C}_{i,\,j}}{dt} = \delta\,(C_{i,\,j} - \overline{C}_{i,\,j}) \qquad (64)$$

where

$$\delta = \frac{\overline{D}\,\overline{A}}{\overline{l}\,Q_j} \qquad (65)$$

The two parameters f_1 and δ must of course be evaluated in terms of the effect they have on the behavior of the model.

Equations (64) and (65) were used to simulate the response of a packed

bed to step forcing of inlet tracer concentration. The equations were solved numerically on the IBM-704 digital computer with various values of f_1 and δ for a one-dimensional model (that is $M = 1$) consisting of 100 stages in series. The inlet stream condition was

$$\phi_{0,1} = 0, \quad -\infty < t < 0$$

$$\phi_{0,1} = 1, \quad t \geq 0$$

(The stages contained zero tracer initially, and at time $t = 0$ the inlet tracer concentration was step changed to 1.0.) The computer was programmed to print the concentrations in a specified group of stages at a number of finite time steps during the passage of the main concentration wave through the group. Again the results from the stage model are most readily compared with experimental data with the differential material balance 1. When solved for N_{Pe_x} the applicable form of (1) becomes

$$N_{Pe_x} = \frac{\dfrac{\partial^2 C}{\partial x^2}}{\dfrac{\partial C}{\partial x} + \dfrac{\partial C}{\partial t}} \qquad (66)$$

Upon substitution of finite difference approximations for the derivatives this may be written as

$$N_{Pe_x}]_{i,l} = P_x(\Delta x, \Delta t)\, C_{i,l} \qquad (67)$$

The j subscript on C is no longer necessary, since the model is one dimensional. The l subscript refers to the finite time axis $t = l\,\Delta t$. The results of applying P_x to various solutions are shown in Table 3. For given f_1 and δ, N_{Pe_x} was found not to depend on l. The values given in Table 3 were calculated for the l which gave a maximum for $\partial^2 C/\partial x^2$. It is also seen that N_{Pe_x} does not vary significantly with i, at least for $i > 60$, which indicates that this simple capacitance correction should apply to most beds encountered in practice. It may be noted that the available measurements fit the relationships

$$\frac{1}{N_{Pe_x}} = \frac{1}{2} + \frac{(f_1)^2}{\delta} \qquad (68)$$

The parameter δ bears at least a dimensional similarity to the Taylor Peclet number, which characterizes Taylor axial spreading in pipe flow. Equation (68) would indicate that the reciprocals of the two types of axial Peclet numbers are additive.

For a physically acceptable value of f_1 (0.9 perhaps) the difference between measured N_{Pe_x} for gases and liquids can be produced by varying δ by a factor of the order 10^3. For given flow conditions δ should depend only on $\overline{D}$, the tracer diffusivity in the total fluid. Thus a thousandfold variation in $\overline{D}$, which is the order of the difference between gas and liquid phase molecular diffusivities, can account for the anomaly in N_{Pe_x}.

SUMMARY

The foregoing analysis serves to establish the finite stage model as a valid representation of the flow environment produced in a packed bed. The basic model was shown to predict the axial and radial mixing observed experimentally for gaseous systems in well-developed turbulent flow ($N'_{Re} > 100$). It was seen that the radial and axial Peclet numbers to be produced by the model may be adjusted independently to agree with specified characteristics of an arbitrary system. A further degree of freedom is also available in the form of a simple capacity effect, which allows the prediction of different N_{Pe_x} for gases and liquids under dynamic operating conditions.

The heat and material balances derived for a stage in the model are first-order, ordinary differential equations in the dynamic case. The balances reduce to purely algebraic form in the steady state. Solution of transient flow problems for an entire bed involves sequential integration of the balance equations which are necessarily of initial-value nature. This process offers numerous mathematical advantages over the techniques required to solve two-dimensional boundary-value problems in partial differential equations, even in the simple flow systems investigated in this part of the paper. In the second part, where chemically reactive systems are of particular interest, these advantages are shown to be decisive.

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NOTATION

Subscripts

- i = row of stages or axial position in finite-difference mesh ($0 \leq i \leq N$)
- j = radial position of stage in a given row ($0 < j \leq M$)
- l = position in finite-time mesh ($l > 0$)
- f = fractional wall stage
- o = standard (inlet and/or center line stage) value of a function

Independent Variables

- x = dimensionless axial length (based on d_p)
- r = dimensionless radial length (based on d_p)
- t = dimensionless time length (based on d_p/v)
- $\overline{t}$ = dimensionless time, redefined by Equation (39)
- t^* = dimensionless time, redefined by Equation (54)
- t' = real (dimensional) time

Dependent Variables

- C = dimensionless concentration (based on C_o)
- T = dimensionless temperature (based on T_o)
- $\overline{T_w}$ = dimensionless wall temperature (based on T_o)
- $\overline{C}$ = dimensionless concentration in the capacity volume (based on C_o)

Dynamic Moduli

- N'_{Re} = modified Reynolds number
- N_{Pe_x} = effective axial Peclet number ($= d_p v/D_x^{(t)}$)
- N_{Pe_r} = effective radial Peclet number ($= d_p v/D_r^{(t)}$)
- N_{Pe_L} = effective axial Peclet number based on bed length ($= Lv/D_x^{(t)}$)
- N_{ST_W} = Stanton number for wall heat transfer

General Roman

- A = cross-section area of a stage, sq. ft.
- A_w = wall area of a stage, sq. ft.
- $\overline{A}$ = area of diffusional surface between capacitance and main parts of a stage, sq. ft.
- C_p = molar heat capacity of the total fluid, (B.t.u./lb. mole °F.)
- C_s = heat capacity of the packing spheres (B.t.u./lb. — °F.)
- D = tube diameter, (ft.)
- $\overline{D}$ = molecular diffusivity in characteristic of the capacity effect in a stage, (sq. ft./hr.)
- $D_r^{(t)}$ = radial component of effective turbulent diffusivity, (sq. ft./hr.)
- $D_x^{(t)}$ = axial component of effective turbulent diffusivity, (sq. ft./hr.)
- d_p = packing sphere diameter
- $f, \overline{f}$ = arbitrary functions
- f_1 = fraction of stage volume not in the capacity effect

$g, \bar{g}$ = arbitrary functions
G_M = molar velocity, (lb. mole/sq. ft.-hr.)
h_w = wall heat transfer coefficient, (B.t.u./hr.-sq. ft. — °F.)
K = arbitrary dimensionless constant
L = tube (bed) length, (ft.)
$\bar{l}$ = diffusional path length characteristic of the capacity effect in a stage
M = number of stages in a radial row, or dimensionless tube radius (based on d_p)
N = number of rows of stages in a bed, or dimensionless bed length (based on d_p)
P_x, P_r = finite-difference operators
Q = total volumetric throughput in a stage, (cu. ft./hr.)
V = stage volume, (cu. ft.)
v = axial fluid velocity based on open area for flow, (ft./hr.)

General Greek

β = dimensionless coefficient in heat balance equations
δ = dimensionless diffusion parameter characteristic of the capacity effect in a stage
ϵ = void fraction of the packed bed
μ_F = dynamic viscosity of the external field, (lb./ft.-hr.)
ρ_F = molar density of the external field, (lb. mole/cu. ft.)
ρ_s = density of the packing spheres, (lb./cu. ft.)
ϕ = dimensionless average inlet concentration to a stage
ψ = dimensionless average inlet temperature to a stage

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A Computational Model for Predicting and Correlating the Behavior of Fixed-Bed Reactors:

II. Extension to Chemically Reactive Systems

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The ability of the finite stage model to represent the macroscopic physical behavior of an unreactive external field was established in part I of this paper (3). On this basis the model may now be evaluated as a framework for the formulation of more complex packed-bed problems. In particular the means and effect on the model of introducing chemical reaction in general form are of interest.

Hereafter the packing spheres are considered to be porous and catalytically active. The reactions which take place on the available surface are assumed to proceed with appreciable heat evolution (or absorption) at rates which vary exponentially with temperature. These heat effects necessitate, among other things, the simultaneous consideration of heat and component material balances for the external field. A reaction rate expression depending on both temperature and concentration must appear, either directly or indirectly, in all the balances; the particular term in which the effect of reaction rate is felt is referred to as the *coupling term.*

This type of physical-chemical coupling between balances is perhaps the most important single characteristic of nonisothermal reactive systems, in that it effectively determines the behavior of such systems both statically and dynamically. Moreover the form of the coupling term is in general such that analytical solutions to the balance equations are not obtainable. The availability of practical numerical procedures for solving the expanded equations of a model is thus a primary consideration.

The nature of the coupling term depends upon a combination of physical and chemical kinetic factors. In a given reactor problem any of the following serial rate mechanisms may be important at a particular position in the reactor:

1. Transport of chemical species and heat of reaction through the interfacial resistance between the external field and the catalyst spheres.

2. Diffusion of reactants and products through the pore matrix of the spheres and conduction of heat through both pore fluid and solid structure of the spheres, between the surface of the spheres and the actual reaction sites.

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