$g, \bar{g}$ = 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**

$\beta$ = dimensionless coefficient in heat balance equations
$\delta$ = dimensionless diffusion parameter characteristic of the capacity effect in a stage
$\epsilon$ = void fraction of the packed bed
$\mu_F$ = dynamic viscosity of the external field, (lb./ft.-hr.)
$\rho_F$ = molar density of the external field, (lb. mole/cu. ft.)
$\rho_s$ = density of the packing spheres, (lb./cu. ft.)
$\phi$ = dimensionless average inlet concentration to a stage
$\psi$ = 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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3. Surface chemical reaction rate at the sites.

Although any one of these may be the absolutely limiting rate step under certain physical conditions, a general statement of a reactor problem must allow for the simultaneous importance of any two, or even all three. Such a statement obviously entails the writing of balances for sphere elements associated with every point in the external field. At positions where rate step 2 is predominant the dimension of the problem is increased even in the favorable case where the elements may be considered one dimensional.

The expression to be introduced for the surface reaction rates will in general be a function of the temperature and the concentrations of all reactants and products at the site. It is apparent that if stoichiometric relationships among the components are available, not all the component concentrations are independent. The conditions under which stoichiometry of the feed stream may be assumed to hold everywhere have been given by Baron (2). His analysis, based on a differential balance model of the type reviewed in part I, showed that all component concentrations except that of the limiting reactant can be eliminated from the rate expression for a single reaction. In the more general case of *P* independent reactions the problem reduces to the simultaneous solution of *P* limiting component material balances and the heat balance, again under favorable circumstances. The remaining (*K*-*P*) concentrations follow from stoichiometry.

A number of conditions may exist in a reactive external field which tend to invalidate the assumptions made in deriving the models of part I. All of them owe their origin to heat effects; qualitatively the more important of these are:

1. Radial temperature gradients when the tube wall is a nonadiabatic boundary.
2. Radial variation in local reaction rates resulting from 1 and the exponential temperature dependence of the rates.
3. Radial variation in density and its axial derivative in gaseous systems caused by 1 and 2, especially where the reactions proceed with net changes in the number of moles present.
4. Nonstoichiometric accumulation in the unsteady state. If condition 3 and 4 are of appreciable magnitude, the stoichiometric relationships of the feed stream cannot be assumed to hold throughout the external field. Although solution of the differential balance model equations would be complicated by this eventuality, the effect on the finite stage-model equations is not serious, as will be seen later.

The possibility of significant radial variation in density tends to invalidate the assumption of constant mass velocity which was made in part I. The finite stage model would have to be expanded to include some form of momentum balance if the effect of nonconstant density on the velocity profile were to be included in an implicit manner. It is in fact possible, under certain conditions, to write macroscopic momentum balances for each stage in the model. One result is the appearance of a radial component of mass velocity from each stage. This has the unfortunate effect of destroying the independence of the equations for stages at a given axial position and thus complicating the numerical solution of the model considerably.

Calculations based on the expanded model would be of theoretical interest only, since no experimental data is available for comparison. Consequently constant density will be assumed in the discussion to follow. However both fluid and packing property values may under normal conditions be considered insensitive functions of temperature and concentration, at least when compared with the coupling term. It is assumed that the magnitudes of the derivatives of the various property-value parameters with respect to the dependent variables are much smaller than the magnitudes of the parameters themselves. Convergence of certain iterative corrections in the numerical solution of the model equations is taken to be guaranteed by this property, so that constant property values will be assumed.

## PARTICULAR FORMS OF THE COUPLING TERMS

With these assumptions the balances for the *k*th component in the *i,j*th stage are

$$\phi_k - C_k + R_k\,(C_1, C_2, \ldots C_K; T) = \frac{dC_k}{dt} \tag{69}$$

and

$$\psi - T + R_T\,(C_1, C_2, \ldots C_K; T) = \frac{dT}{dt} \tag{70}$$

The *i, j* subscripts have been deleted for clarity. Each stage may now be considered to contain $6(1-\epsilon)(2j-1)$ catalyst spheres, all of which are in equivalent positions in the original packed bed which the stage model simulates.

In the general situation where all the rate steps mentioned earlier are of potential importance, heat and material balances for this composite sphere element must be solved in conjunction with the external field balances for each stage. The internal problem will not be considered here in detail; that is no formulation of the sphere-element balances will be proposed. It need only be stated that the pore-diffusion and surface-rate mechanisms are contained in these balances. However the boundary conditions at the surface of the sphere element are needed for subsequent arguments. These may be written as

$$\left[\frac{\partial C_k(s)}{\partial \rho}\right]_{i,j} = \{N_{Sck}\,[C_k - C_k(s)]\}_{i,j} \tag{71}$$

and

$$\left[\frac{\partial T(s)}{\partial \rho}\right]_{i,j} = \{N_{Nu}\,[T - T(s)]\}_{i,j} \tag{72}$$

$T(s)$ and $C_k(s)$ are values of these functions at the surface of the sphere element, that is on the inside of a fictitious interfacial film which separates the sphere element of the *i, j*th stage from its external field.

Thus the coupling terms $R_k$ and $R_T$ need only express the material and heat transport across the film in a manner consistent with (71) and (72). The external field balances may therefore be written

$$\phi_k - C_k + N_{STk}[C_k(s) - C_k] = \frac{dC_k}{dt} \tag{73}$$

$$\psi - T + N_{ST}\,[T(s) - T] = \frac{dT}{dt} \tag{74}$$

$N_{ST}$, $N_{STk}$, $N_{Sck}$, and $N_{Nu}$ will in general be functions of temperature and concentration, but of the type prescribed earlier; that is they may be assumed constant in a first approximation and subsequently corrected interatively.

In the steady state (74) may be solved for *T* to give

$$T = \frac{\psi + N_{ST}\,T(s)}{1 + N_{ST}} \tag{75}$$

This result may be used to eliminate *T* from (72), the result being

$$\left[\frac{\partial T(s)}{\partial \rho}\right]_{i,j} = \left\{N_{Nu}\left[\frac{\psi - T(s)}{1 + N_{ST}}\right]\right\}_{i,j} \tag{76}$$

By analogous manipulation (73) becomes

$$\left[\frac{\partial C_k(s)}{\partial \rho}\right]_{i,j} = \left\{N_{Sck}\left[\frac{\phi_k - C_k(s)}{1 + N_{STk}}\right]\right\}_{i,j} \tag{77}$$

Since $\psi$ and $\phi_k$ are considered to be known functions (from solutions of the finite stage balances for row $i-1$), the internal problem may be solved independently. $T$ and $C_k$ then follow from (75) and the equivalent steady state material balance.

Similar arguments hold for the unsteady state or transient condition. The right side of (70) for example may be replaced by a finite difference approximation of arbitrary order. It is assumed that $T$ is known at times up to $t = l\Delta t$ on a finite time axis and unknown at $t = (l+1)\Delta t$. Equation (70) becomes in symbolic differenced form $T_{l+1} \doteq U\,[N_{ST}; T_{l-m}; \psi_{l-m+1};$

$$T(s)_{l-m}; T(s)_{l+1}] \quad (78)$$

$$m = 0, 1, 2, \ldots\ldots$$

in which only $T(s)_{l+1}$ is unknown. In equivalent manner the boundary condition (72) is approximated as

$$\overline{\frac{\partial T(s)}{\partial \rho}} \doteq V\,[N_{Nu}; T_{l+1}; T_{l-m}; T(s)_{l-m+1}] \quad (79)$$

where the left side is understood to be an average over the $(l+1)$ time step. On substitution of (78), (79) becomes

$$\overline{\frac{\partial T(s)}{\partial \rho}} \doteq W[N_{ST}; N_{Nu}; \psi_{l-m+1}; T_{l-m}; T(s)_{l-m+1}] \quad (80)$$

which contains no unknown values of $T$. With (80) and the equivalent material boundary conditions, the sphere element balances may be solved for the $(l+1)$th time step. $T_{l+1}$ and $(C_k)_{l+1}$ follow from (78) and the analogous expressions for the concentrations.

The purpose of the foregoing discussion is to show that accounting for internal rate steps does not disturb the sequential character of the solution of the external problem. It is assumed hereafter that the surface reaction rate step is absolutely controlling; that is the internal surface is uniformly accessible to the external field. Also solid temperature is considered equal to fluid temperature in each stage. Basing later arguments on these assumptions one implies that the internal problem can be readily solved by using straightforward numerical procedures, which is not necessarily the case. Especially in the unsteady state, time required for numerical solution may be greater by a factor of 100 or more when the internal problem is included. This fact limits the practical value but not the applicability of the model.

## STOICHIOMETRIC LIMITATIONS

It was pointed out earlier that the stoichiometric relationships of the feed stream could be assumed to hold throughout the external field only under certain conditions. The assumptions of constant molar and mass density are sufficient to satisfy these conditions in the steady state, although nonstoichiometric accumulation is still possible under transient conditions. However such universal relationships are not required by the finite stage model. For each independent reaction occurring there will be a locally limiting reactant in the combined feed stream to a given stage. If nonstoichiometric accumulation in the stage is ignored as a first approximation, it follows for a single reaction that

$$\phi_k - C_k = \left(\frac{\nu_k}{\nu_\xi}\right)(\phi_\xi - C_\xi) \quad (81)$$

where $\nu_\xi$ is the stoichiometric coefficient of the limiting reactant. All other concentrations may be eliminated from the coupling term in the material balance for component $\xi$ by using the linear relationships (81); that is

$$R_\xi(C_1, C_2, \ldots\ldots C_\xi, \ldots\ldots C_K; T)$$
$$= R_\xi(C_\xi; \phi_1, \phi_2, \ldots\ldots \phi_K; T) \quad (82)$$

Thus only one material balance has to be solved simultaneously with the heat balance. The $C_k$ $(k \neq \xi)$ follow from (81). By similar reasoning all but $P$ concentrations may be eliminated from $P$ properly chosen coupling terms in the more general case of $P$ independent reactions. This latter situation will not be considered here, since the algebraic complications introduced are not balanced by any increase in generality of the analysis. A first-order, irreversible, effectively homogeneous reaction is sufficient for later purposes. The coupling terms may be written in explicit form as

$$R_k = -C(k\,e^{-E/T}) \quad (83)$$

and

$$R_T = \lambda C(k\,e^{-E/T})$$

In the specific examples to follow $\lambda$ is considered positive (exothermic reaction) and independent of temperature and concentration, as are $\beta$ and $E$. It was assumed earlier that the variation of property values with the dependent variables is such that iterative corrections converge. The numerical procedures for making these corrections are straightforward and will not be discussed here.

## NUMERICAL SOLUTION FOR A TYPICAL REACTIVE SYSTEM

The balance equations to be solved for a suitable choice of parameters are

$$\phi_{i-1,j} - C_{ij,}(1+k\,e^{-E/T_{i,j}}) = \frac{dC_{i,j}}{dt} \quad (84)$$

$$1 \leq i \leq N; 0 < j \leq M$$

and

$$\psi_{i-1,j} - T_{i,j} + \lambda\,C_{i,j}\,k\,e^{-E/T_{i,j}} = \beta\frac{dT_{i,j}}{dt} \quad (85)$$

$$1 \leq i \leq N; 0 < j < M$$

For $j = M$, (85) must include the effect of heat transfer at the wall. If the wall heat transfer coefficient $N_{ST_W}$ is considered constant

$$\left(\frac{\psi_{i-1,M} + N_{ST_W}\,T_{W_i}}{1 + N_{ST_W}}\right) - T_{i,j}$$
$$+ \left(\frac{\lambda}{1 + N_{ST_W}}\right) C_{i,M}\,k\,e^{-E/T_{i,M}}$$
$$= \left(\frac{\beta}{1 + N_{ST_W}}\right)\frac{dT_{i,M}}{dt} \quad (86)$$

which is of the same form as (85). The inlet and initial conditions which complete the specification of the system are

$$\phi_{o,j} = \phi_o(t), \psi_{o,j} = \psi_o(t), \; T_{W_i} = T_{W_i}(t)$$

$$C_{i,j}(0) = C(i,j) \qquad T_{i,j}(0) = T(i,j)$$

Equations (84) and (85) represent the finite stage-model formulation of a system which has been stripped of a number of complicating factors, namely variable mass and molar density, internal pore diffusion and surface film transport as contributing rate steps, the complex homogeneous kinetic expressions associated with multiple higher order (that is other than first order) reactions, and property values which vary with temperature and concentration.

On the other hand the equations are still sufficiently general to account for many of the major physical effects in a reactive system, which are turbulent, radial, and axial mixing, thermal coupling of heat and material balances by a realistic rate expression, and heat transfer through the tube wall.

The particular system parameters chosen for the example are

$$2M = 11 \qquad \beta = 2.5 \qquad E = 10$$
$$\lambda = 1$$
$$N = 60 \qquad N_{ST} = 2 \qquad \left(\frac{e^E}{k}\right) = 250$$

Two cases have been evaluated numerically on an IBM-704 digital computer. The first, a steady state case, had as boundary conditions

$$\phi_o(t) = \psi_o(t) = T_{W_i}(t) = 1$$

The appropriate forms of (84) and (85) are

$$\phi_{i-1,j} - C_{i,j}\,(1 + k\,e^{-E/T_{i,j}}) = 0 \quad (87)$$

and

$$\psi_{i-1,j} - T_{i,j} + C_{i,j}\,\lambda\, e^{-E/T_{i,j}} = 0 \quad (88)$$

Equation (87) may be used to eliminate $C_{i,j}$ from (88), the rearranged result being

$$\psi_{i-1,j} - T_{i,j} + \frac{\lambda\,\phi_{i-1,j}}{\dfrac{e^{E/T_{i,j}}}{k} + 1} = 0 \quad (89)$$

The numerical problem reduces to that of locating the root of a simple transcendental equation. Once the value of $T_{i,j}$ which satisfies (89) is found, $C_{i,j}$ can be obtained from (87). Since the root of (89) may be determined to any desired accuracy (the number of digits in a machine word serving as a practical limitation), no errors arise in the steady state case beyond those resulting from the assumptions of the finite stage model itself.

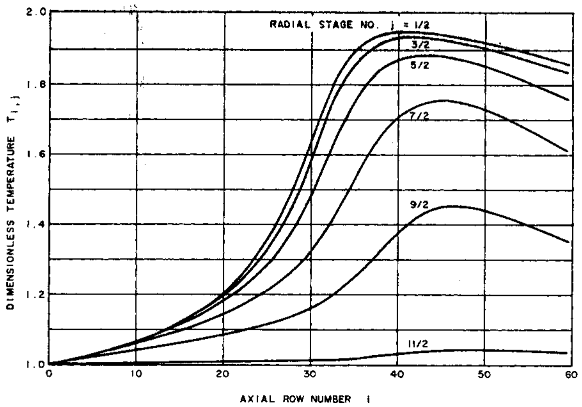

**Fig. 3. Longitudinal temperature profiles at various radial position, static system.**

The solutions of (87) and (88) for $i$ odd, $j$ = 1/2, 3/2, . . . . . 11/2, are shown on Figures 2 and 3. Curves were drawn through the points for each value of $j$ to clarify the results.

Calculation of $T_{i,j}$ and $C_{i,j}$ for the 360 stages in the system required 35 sec. on the IBM-704. This elapsed time is equivalent to about 400 multiplications (or divisions) per stage. Seven-place accuracy was obtained in all answers by iteration, with a Newton-Raphson formula with third-order correction term (*4*) used.

The values of the parameters $E$, $k$, and $\lambda$ used here are such that (89) possesses a single root for each stage in the system. It may be shown (*1*) that this equation has three distinct roots for certain combinations of $E$, $k$, and $\lambda$. The fact that only two of these roots correspond to physically stable operation of a stage cannot be shown from analysis in the steady state. Moreover the choice between the two physically acceptable roots depends upon the manner of approach to steady state. These difficulties may be avoided by using the dynamic model equations to simulate start-up as part of a design calculation. If the proper initial conditions are employed, every stage must approach its correct steady state operating condition.

A second case was run with the same parameter values to show the response of the system to an idealized disturbance of an inlet variable. The results of the first case were used as initial conditions for all stages in the model. At $t$ = 0, $\phi_o$ was changed from 1.0 to 0.75. All other conditions remained constant; that is

$$\begin{aligned} \phi_o(t) &= 1, & -\infty < t < 0 \\ \phi_o(t) &= 0.75, & 0 \leq t < +\infty \\ \psi_o(t) &= T_{W_i}(t) = 1, & -\infty < t < +\infty \end{aligned}$$

Since (85) and (86) are ordinary differential equations, a variety of numerical integration techniques are applicable. The particular one used here was chosen for its simplicity and the consequent ease with which it could be programed for a digital computer. The method is numerically stable for any reasonable value of $\Delta t$ on a finite time axis $t = l\Delta t$, the only limitation in the size of $\Delta t$ being the allowable truncation error.

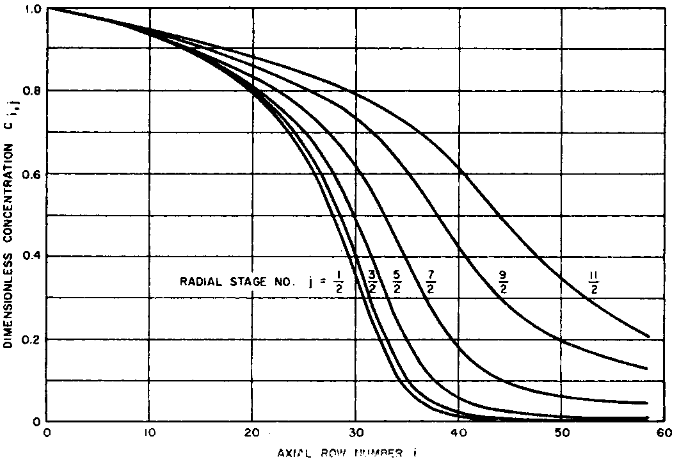

**Fig. 2. Longitudinal concentration profiles at various radial positions, static system.**

If first-order central difference approximations about the point $t = (l + \frac{1}{2})\Delta t$ are substituted for the derivatives, (84) and (85) may be written

$$\overline{\phi_{i-1,j} - C_{i,j}(1 + k\, e^{-E/T_{i,j}})} \doteq \frac{C_{i,j,l+1} - C_{i,j,l}}{\Delta t} \quad (90)$$

and

$$\overline{\psi_{i-1,j} - T_{i,j} + C_{i,j}\,\lambda\, k\, e^{-E/T_{i,j}}} \doteq \beta\left[\frac{T_{i,j,l+1} - T_{i,j,l}}{\Delta t}\right] \quad (91)$$

The left-hand sides are averaged over the $(l+1)$th time step. The $i$ and $j$ subscripts are deleted hereafter to avoid confusion. With simple arithmetic averages introduced (except for the exponential term) (90) and (91) become

$$\frac{\phi_l + \phi_{l+1}}{2} - \frac{C_l + C_{l+1}}{2}\left[1 + k\overline{(e^{-E/T})}\right] \doteq \frac{C_{l+1} - C_l}{\Delta t} \quad (92)$$

and

$$\frac{\psi_l + \psi_{l+1}}{2} - \frac{T_l + T_{l+1}}{2} + \frac{C_l + C_{l+1}}{2}\lambda\, k\overline{(e^{-E/T})} \doteq \beta\left(\frac{T_{l+1} - T_l}{\Delta t}\right) \quad (93)$$

Equation (92) may be solved algebraically for $C_{l+1}$ and the result used to eliminate this unknown from (93). After rearrangement the final equation is

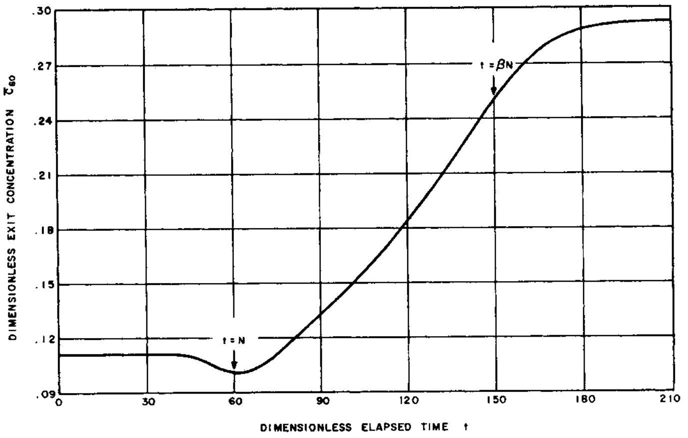

Fig. 4. Outlet concentration response to step forcing of inlet concentration.

$$T_{l+1} \doteq \frac{\left(\frac{2\beta}{\Delta t} - 1\right) T_l + \psi_{l+1} + \psi_l + \lambda \left[ \frac{\frac{4}{\Delta t} C_l + \phi_l + \phi_{l+1}}{(2/\Delta t + 1) - + 1 \frac{\overline{e^{E/T}}}{k} + 1} \right]}{\frac{2\beta}{\Delta t} + 1} \tag{94}$$

Everything on the right side of (94) is known except $\overline{e^{E/T}}$. If $\Delta t$ is not too large

$$\overline{e^{E/T^{(1)}}} \cong e^{E/T_l} \tag{95}$$

gives a reasonable first approximation, which allows calculation of $T^{(1)}{}_{l+1}$ from (94). $\overline{e^{E/T}}$ may be corrected by the formula

$$\overline{e^{E/T^{(m+1)}}} = e^{\frac{(E/T_l + E/T^{(m)}{}_{l+1})}{2}} \tag{96}$$

The iteration converges very rapidly for the small value of $\Delta t$ used in the second case. The final stationary value of $\overline{e^{E/T}}$ is then used in (92) to calculate $C_{l+1}$.

Figures 4 and 5 show the resulting output concentration and temperature as a function of $t$ for the second case. The variables plotted are volume averages for the 60th row, given by

$$\overline{f_{60}} = \frac{\sum_{j=1}^{5} (2j-1)\, f_{60,\,j} + \frac{21}{4} f_{60,\,11/2}}{\sum_{j=1} (2j-1) + \frac{21}{4}} \tag{97}$$

where $\overline{f}$ is either $C$ or $T$. The terms outside the summations are for the wall stage, which was fractional in the even rows. Calculation time on the IBM-704 was about 17 min. to $t = 217.5$, with $\Delta t = 0.25$.

The effect of coupling between heat and material balances is apparent in Figures 4 and 5. If no coupling were present ($\lambda = 0$ for example), a fluctuation in inlet concentration would show up at the outlet near $t = 60$, the piston-flow residence time for material. Indeed a small pseudolinear response begins to appear just before $t = 60$. The major response however occurs much later since the mean residence time for heat is $60\beta$, $t = 150$ in this case. Temperature disturbances caused by changing concentration travel through the model at the slower rate $\nu/\beta$, as both external field and catalyst spheres supply heat capacity.

The ambiguity of response exhibited by both variables indicates that a conventional control system would be totally inadequate. Both the magnitude and the direction of output changes depend on the nature of the forcing, the values of the parameters, and the history of every point in the system.

The possible use of the finite stage model in conjunction with an anticipating or feed-forward control system is discussed in the later section on applications.

## COMPARISON OF FINITE STAGE MODEL WITH EQUIVALENT PARTIAL DIFFERENTIAL EQUATIONS

The differential balance model discussed in part I may be expanded to apply to the simple example which was just solved by means of the finite stage model approach. The differential heat and material balances are

$$\frac{1}{N_{Pe_x}} \frac{\partial^2 C}{\partial x^2} + \frac{1}{N_{Pe_r}} \left[ \frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} \right] - \frac{\partial C}{\partial x} - C\, k\, e^{-E/T} = \frac{\partial C}{\partial t} \tag{98}$$

and

$$\frac{1}{N_{Pe_x}} \frac{\partial^2 T}{\partial x^2} + \frac{1}{N_{Pe_r}} \left[ \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right] - \frac{\partial T}{\partial x} + \lambda\, C\, k\, e^{-E/T} = \beta \frac{\partial T}{\partial t} \tag{99}$$

The boundary and initial conditions given in part I also apply to this system. The equations are still of the boundary-value type but are no longer linear. They have not been solved either analytically or numerically to date.

Unfortunately it is impossible even to estimate the time requirements for a numerical solution of these equations, since the numerical stability (and rate of convergence where iteration is required) of applicable procedures cannot be predicted. However certain general observations can be made regarding any method employed. Finite differencing of all derivatives would be required, resulting in a three-dimensional array of mesh points. The differenced forms of (98) and (99) written for each mesh point would

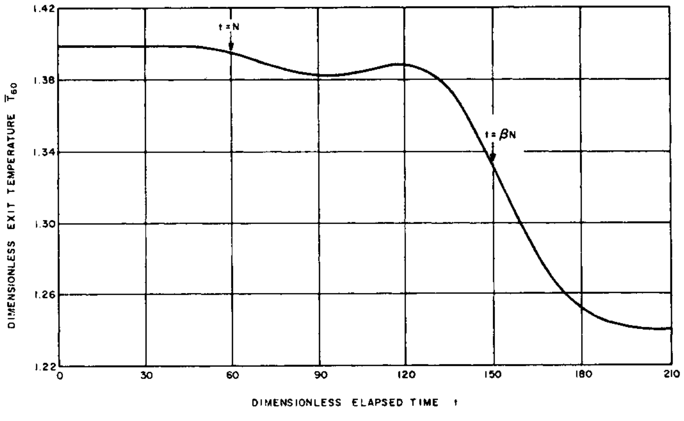

Fig. 5. Outlet temperature response to step forcing of inlet concentration.

still be coupled by nonlinear rate terms. Because of the boundary conditions in both $x$ and $r$ directions the entire two-dimensional set of equations for each time plane would have to be solved simultaneously, unless explicit techniques were used. The latter alternative however is characterized by acute stability problems unless the finite time increment is sufficiently small. In any case the total number of calculations necessary to proceed a physically meaningful distance along the time axis would be very large.

It is apparent from this that the use of the differential balance for more complex systems offers little promise for successful numerical solution. Inclusion of kinetic mechanisms within the packing for example would aggravate the problem of stability and/or convergence rate, since a new dimension would be added to the finite difference grid. Differenced balance equations for an associated sphere element would be coupled through boundary conditions to the differenced external field balances at every point in the original three-dimensional grid. No separability of internal and external problems is to be expected.

Since (98) and (99) have not been solved, no direct measurement of agreement between solutions given by the two models can be made. As a means of indirect comparison the stage-model solution obtained for the second case above could be differentiated numerically at various points and substituted into (98) and (99). However since this was essentially the procedure used in part I to obtain the constant values of $N_{Pe_r}$ and $N_{Pe_x}$ produced by the finite stage model, it need not be repeated. As long as the chemical reactions are not so rapid as to invalidate the assumption of small functional variation over a length $d_p$, a solution obtained from the finite stage model will essentially satisfy the differential balance model. In the presence of extensive reactions it woud be a priori expected that the models will disagree. At the present state of knowledge it is difficult to say which model would then be more representative of actual conditions.

## APPLICATIONS OF THE FINITE STAGE MODEL

The purpose of part II of this paper has been to indicate both the means of including chemical reaction in the finite stage model and the computational advantages of the resulting formulation over the conventional partial differential equation approach. Solution of quite general external field problems was seen to involve at most the numerical integration of a set of simultaneous, first-order, ordinary differential equations.

Three categories of engineering activity offer possible applications for the finite stage model. These are a priori design of fixed bed reactors, analysis of data from fixed bed processes, and control of nonlinear fixed bed systems. In lieu of conclusions some specific uses in each of these areas are suggested. It should be emphasized that experimental proof of the applicability of the finite stage model to actual reactive systems is almost entirely lacking. The following remarks are therefore admittedly speculative in nature.

Scale up, optimization, and determination of stability or parametric sensitivity are steps in a design calculation in which the finite stage model could be employed. The model accounts for the various factors which change with the dimensions of a fixed bed, so that at least some of the experimental steps in an incremental scale up might be avoided. The model representation of the full-size design could be subjected to optimization by means of recently developed statistical techniques. The final optimized design would then be checked for stability and sensitivity by dynamic perturbation of the model. Linearization was seen not to be necessary for such unsteady state calculations.

Various factors are present in experimental integral reactors and mass exchange columns which tend to obscure the basic rate mechanisms. The model furnishes a means of eliminating certain of these effects, at least in an implicit manner. Turbulent mixing, dynamic bed capacitance, variation of fluid and bed property values with dependent variables, and heat coupling may all be taken into account and thus removed from the final analysis of actual physical or chemical kinetics. Since analytical solution of the model equations is normally not possible, assumed kinetic mechanisms would have to be inserted in the model and experimental results compared with the numerical solutions obtained.

Finally the finite stage model qualifies for consideration as one component of an open-loop computer control system for a nonlinear fixed-bed process. The simple unsteady state example calculated earlier serves to show that closed-loop control of such processes is probably impractical. The calculation also indicates that the complete model could not be used as a real-time simulating tool. A file of predicted system behavior would have to be computed before start-up, to be used as an initial basis for decisions by the real-time components. Depending on the complexity and stability of the process adaptive or corrective functions might be necessary in the control system to expand the file and keep it up to date. The parameters of the model would of course be corrected concurrently.

## NOTATION

### Subscript

$\xi$ = limiting reactant in a reaction

### Independent Variables

$\rho$ = dimensionless sphere radial position (based on $d_p/2$)

### Dynamic Moduli

$N_{ST}$ = Stanton number for heat transfer

$N_{ST_k}$ = Stanton number for mass transfer of the $k$th component

$N_{Nu}$ = Nusselt number

$N_{Sch}$ = Schmidt number for the $k$th component

### General Roman

$E$ = dimensionless activation energy ($= E_{act}/RT_o$)

$E_{act}$ = activation energy (B.t.u./lb. mole)

$\Delta H_R$ = heat of reaction, (B.t.u./lb. mole)

$k$ = dimensionless (homogeneous) rate constant ($=k_\infty d_p/v$)

$k_\infty$ = first-order homogeneous rate constant at infinite temperature (hr.$^{-1}$)

$K$ = total number of chemical species in a system

$M_R$ = direct radial mass flow (lb./hr.)

$P$ = number of independent chemical reactions

$R_k$ = coupling term in the $k$th component material balance

$R_T$ = coupling term in the heat balance

$U,V,W$ = unspecified functions

### General Greek

$\eta,\gamma$ = temperature and concentration dependent coefficients (dimensionless)

$\pi$ = pressure in a row of stages

$\nu_k$ = stoichiometric coefficient of $k$th component in a reaction

$\lambda$ = exothermicity group (dimensionless) ($= -\Delta H_r C_o/C_p \rho_F T_o$)

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