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Modeling Transient Tracer Studies in Plug-Flow Reactors

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The use of plug-flow reactors is common for kinetic studies in heterogeneous catalysis. Recently, transient tracing has been found to be advantageous in providing additional mechanistic information above that obtained by customary steady-state kinetics. Despite the advantages of transient tracing, it often suffers from incorrect data analysis in the case of plug flow because of failure to take into account the formalism needed to model plug-flow transient tracing as contrasted with that required to describe transient tracing in a gradientless recirculating reactor (CSTR). This paper presents a development of the appropriate differential equation system applying to plug-flow studies involving transient isotopic tracing superimposed on an overall steady-state kinetics. Closed mathematical expressions are presented for simple practical cases and used to illustrate important special characteristics of these systems. © 1990 Academic Press, Inc.

INTRODUCTION

Both gradientless and plug-flow reactors (*1, 2*) have been employed without tracers in studies of heterogeneous catalysis. If data are obtained under steady-state operation, a plug-flow reactor is often operated with differential conversion. In this way, an average reaction rate can be assumed and it is possible to avoid integration of an assumed rate expression. Under these conditions, each sample set corresponds to a single reaction rate at fixed temperature, pressure, and concentration of observable reactants and products.

Additional information regarding basic parameters (surface concentration of adsorbed intermediates and step velocities) is obtainable by transient isotopic tracing. The procedure employed (*1*) is the introduction of a step function of traced reactant or product, while at the same time maintaining the total concentration of species unchanged. In this way it is still possible to retain the same kinetics of the steady-state regime provided that isotopic kinetic effects can be neglected. A number of systems have been studied using this procedure (*1*) for reactions conducted in gradientless recirculating (CSTR) reactors using compartmental modeling (*3, 4*). More recently this experimental technique has been applied (*5–8*) to data obtained in plug-flow reactors, but results have been incorrectly interpreted by using compartmental modeling to correlate the data.

There are, of course, additional factors that need to be considered in the design of plug-flow experimental systems to secure satisfactory data. These problems are common in the design of reactors whether or not tracer is employed. What is important here in the context of plug-flow operation is that when a once-through system is employed very accurate chemical analysis will be required as contrasted with recycle operations in gradientless systems where the recirculating stream, which is also the outlet, is sampled. The accuracy and speed of response of analytical equipment such as a mass spectrometer must be considered. Methods of introduction of traced species and removal of samples must avoid causing abrupt changes in system pressure. Dilution of reacting species by an inert carrier gas may be desirable to extend response

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time. The configuration of the catalyst particles and the dimensions of the bed must be such as to minimize intraparticle diffusion and axial mixing effects.

In what follows, we will first present the basic mathematical equations that are required to model plug-flow transient tracing. Next, the relationship between the more conventional compartmental modeling and plug-flow tracing will be considered. Finally the results will be illustrated by providing exact solutions for simple cases involving unidirectional overall reactions by applying the Laplace transform technique.

BASIC PLUG-FLOW EQUATIONS

Let us consider the simplest possible system for a heterogeneous catalytic reaction:

$$A \underset{v_{-1}}{\overset{v_{+1}}{\rightleftarrows}} A\mathrm{l} \underset{v_{-2}}{\overset{v_{+2}}{\rightleftarrows}} B. \qquad (1)$$

This schematic representation consists of a reactant A, producing an intermediate Al (l is a catalyst site), and finally a product B. We wish to model transient tracing for this system in a plug-flow reactor with differential conversion of the reactant A to the product B. It is assumed that the reaction system itself is first brought to steady state. At time $t = 0$, the input of the reactor is switched to one containing a fixed proportion of marked A or B while at the same time maintaining constant the total concentrations of marked plus unmarked species. The fraction of tracer in components A and B is observed until steady-state marking is finally attained.

Figure 1 (not to scale) illustrates the plug-flow reactor in which we focus attention on a Δw increment, where w represents axial position in the bed containing a mass of catalyst W. We will construct mass balances at a given instant of time t for all three of the designated species A, Al, and B. Note that Al is at a fixed position in the bed, contrary to A and B, which are passing through it. Since the mass balances involve two phases, it is necessary to employ a conversion factor so as to have a common basis.

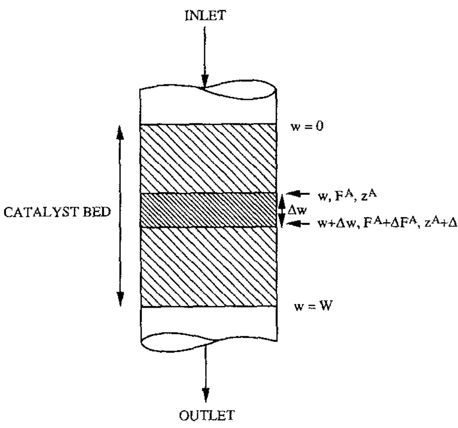

FIG. 1. Plug-flow reactor (A species).

Chemical reaction rates are often written in terms of conversion per unit time and unit mass of catalyst. We will adopt this convention and write conversion in terms of gaseous volumes at standard conditions of temperature and pressure. Thus a simple example for units of velocity would be ml STP/(s · g). Let β be the equivalent dead space; it consists of the volume STP associated with all intra- and interparticulate voids for the entire mass of the catalyst. We assume that the reactor is operated isothermally and isobarically. For purposes of a mass balance, it is necessary to express β in terms of gas volume under standard conditions rather than as actual physical volume. Thus β/W serves to convert concentration of a component A or B from a fraction of the gas phase to the amount of the component per unit mass of catalyst. With these conventions we may derive the following mass balances in the gas phase per unit mass of catalyst.

Let us construct the mass balance for marked A in a section Δw, assuming that v_{+1} and v_{-1} are constant since the reaction is differential throughout the entire catalyst bed. Feed enters the section Δw at a rate F^A and leaves it at a rate $(F^A + \Delta F^A)$ (Fig. 1). At the same time, the fractional marking of A entering the section Δw is z^A and that leaving it is $(z^A + \Delta z^A)$. Thus the net input of marked A from the gas flow through the Δw section is

$$\begin{array}{ll} \text{input} & \text{output} \\ F^A z^A - & (F^A + \Delta F^A)(z^A + \Delta z^A) \end{array}$$

$$\overset{\text{net input}}{= -F^A\,\Delta z^A - z^A \Delta F^A - \Delta F^A \Delta z^A}. \quad (2)$$

At the same time, z^{A1} the fractional marking of $A1$ on the catalyst can be taken at an average constant value. The net input of marked A from the catalyst within the Δw section is thus

$$\begin{array}{ll} \text{input} & \text{output} \\ v_{-1} z^{A1}\,\Delta w - & v_{+1} z^A\,\Delta w \end{array}$$

$$\overset{\text{net input}}{= (v_{-1} z^{A1} - v_{+1} z^A)\,\Delta w}. \quad (3)$$

The contribution from the sum of the processes shown in Eqs. (2) and (3) results in an accumulation per unit time in the Δw section, which may independently be expressed as follows

$$\frac{\beta C^A}{W} \frac{\partial z^A}{\partial t}\,\Delta w = \text{accumulation}. \quad (4)$$

Thus, equating the sum of Eqs. (2) and (3) with Eq. (4) and neglecting the second-order term $\Delta F^A \Delta z^A$, we obtain

$$\frac{\beta C^A}{W} \frac{\partial z^A}{\partial t}\,\Delta w = -F^A\,\Delta z^A - z^A\,\Delta F^A + (v_{-1} z^{A1} - v_{+1} z^A)\,\Delta w. \quad (5)$$

Dividing by Δw and letting Δz^A and Δw approach zero, we obtain

$$\frac{\beta C^A}{W} \frac{\partial z^A}{\partial t} = -F^A \frac{\partial z^A}{\partial w} - z^A \frac{\partial F^A}{\partial w} + v_{-1} z^{A1} - v_{+1} z^A. \quad (6)$$

Since $F^A\,dz^A + z^A\,dF^A = d(F^A z^A)$, Eq. (6) can be written as

$$\frac{\partial F^A z^A}{\partial w} + \frac{\beta C^A}{W} \frac{\partial z^A}{\partial t} = v_{-1} z^{A1} - v_{+1} z^A. \quad (7)$$

In Eq. (7), F^A is a function of w and z^A is a function of both w and t.

In a similar fashion the mass balances corresponding to species $A1$ and B can be constructed. They are as follows:

$$C^{A1} \frac{\partial z^{A1}}{\partial t} = v_{+1} z^A - v_{-1} z^{A1} - v_{+2} z^{A1} + v_{-2} z^B \quad (8)$$

$$\frac{\partial F^B z^B}{\partial w} + \frac{\beta C^B}{W} \frac{\partial z^B}{\partial t} = v_{+2} z^{A1} - v_{-2} z^B. \quad (9)$$

It is readily seen that for more complicated mechanisms the same procedure using material balances can applied. As many partial differential equations are obtained as there are species.

In order to estimate the unknown parameters of such models (i.e., step velocities and surface concentrations) from experimental data, these equations must be solved (either numerically or analytically) in terms of these parameters. For numerical solution, one uses trial values of the parameters to generate predicted tracer concentrations which may be compared with the actual data in order to select the set which, using some suitable criterion, optimizes the goodness of fit.

Before proceeding to the solution of these types of equations, we wish to elaborate the distinction which must be made between models for plug-flow and gradientless recirculating (CSTR) reactors. For this purpose we present in the next section an alternative equivalent way of visualizing the characteristics of models for plug-flow transient tracing.

COMPARISON WITH COMPARTMENTAL MODELS

When a gradientless recirculating reactor is employed instead of a plug-flow reactor, the scheme for interpreting transient tracing is often described as a compartmental model. The resulting model equations are somewhat different from those developed in the previous section for plug-flow. A compartmental model consists of a finite number of well-mixed subsystems, called compartments, which exchange with each other and the environment (*3*). The quantity and concentration of tracer within each compartment may be described by a first-order ordinary differential equation. A

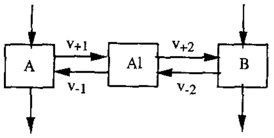

FIG. 2. Simple compartmental model.

compartmental system may be used to model the kinetics of two or more species, in which case different compartments may occupy the same physical space.

Compartmental models are widely used for the modeling of systems in biomedicine, pharmacokinetics, and ecology but applications in chemical engineering are fewer. In the biosciences, data are often obtained by employing small concentrations of radioactive isotopes as tracers. It is possible to describe such experiments by linear models in which flow rates are proportional to quantities in a donor compartment. In the method that we employ (*4*), linearization is accomplished by tracer substitution which allows us to use large concentrations of tracers.

Let us consider the system represented by Eq. (1). In terms of a compartmental model for this reaction occurring in a *gradientless* reactor, the mechanism can be represented as shown in Fig. 2. The compartments are represented by boxes and arrows indicate the exchange of material between compartments or between compartments and the outside.

Three mass balances are involved, corresponding to the three compartments. Note that compartments A and B occupy the same physical space. Physically, a single CSTR accomodates all three compartments. The three ordinary differential equations in time associated with this model are readily available (*4*).

If we wish to extend consideration of this model to data collected in a *plug-flow* reactor, the situation is more complicated because an independent space variable w is involved as well as time. We might visualize the situation as corresponding to a series of compartmental submodels as shown in Fig. 3.

The boxes marked A and B occupy the entire gas space in Δw but they both occupy this space together, as in the simple compartmental model. Gas passes downward through the bed but the species $A1$ exchanges on the catalyst surface which is physically not part of the space occupied by A and B. Thus the increment designated by Δw in the previous section may be transformed into one of a series of compartmental models, each of which consists of three compartments. An alternative way of simulating our model would then be to compute the solution of the corresponding set of ordinary differential equations in time. If we chose to divide the reactor into 10 space increments, this could involve solving a set of 30 first-order ordinary differential equations. Because of the lack of sufficiently detailed appropriate experimental data in the literature for modeling plug-flow experiments, we will not carry out numerical solution of the partial differential equations developed in the previous section or for the equivalent formalism developed in this section. Instead, in the following section, we will confine our attention to analytical solu-

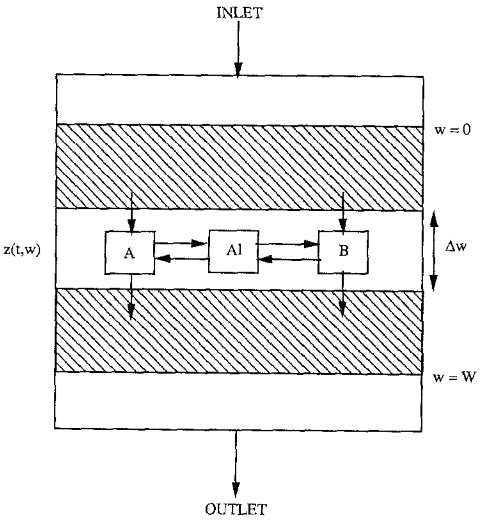

FIG. 3. Extended compartmental model.

tions of several simple cases of practical interest.

SIMPLE UNIDIRECTIONAL REACTIONS

Single Intermediate

Consider again the model described by Eq. (1), but for the unidirectional case where $v_{-1} = v_{-2} = 0$, so that $v_{+1} = v_{+2} = V$:

$$A \xrightarrow{V} A1 \xrightarrow{V} B. \tag{10}$$

Since we are dealing with a differential plug-flow reactor, we assume that C^A and C^B can be expressed as linear functions of the position in the bed w, so that, if for simplicity we have a pure feed of component A with $F^B(0) = 0$, the following relationships apply:

$$F^A(w) = F - V\,w,\ C^A(w) = \frac{F^A(w)}{F},$$

$$F^B(w) = V\,w, \quad C^B(w) = \frac{F^B(w)}{F}. \tag{11}$$

For the purpose of computing the step velocities in a differential reactor, all concentrations are taken as constant and equal to their average value. This is why in what follows we will consider C^{A1} as a constant. This should not be confused with the fact that a nonzero reaction rate implies a change in concentration of reacting species between the input and output of a differential section.

The boundary conditions are as follows. At time $t = 0$, z^A, z^{A1} and z^B are zero for any value of w corresponding to the inside of the reactor. At the entrance of the reactor bed ($w = 0$) a step function z^A of magnitude z_0^A is introduced starting at time $t = 0$.

The solution of the model for the plug-flow reactor corresponding to Eq. (10) has already been reported (*1*),

$$z^A(t, w) = z_0^A\, u\left(t - \frac{\beta w}{FW}\right) \tag{12}$$

$$z^{A1}(t, w) = z^B(t, w) = z_0^A \left\{1 - \exp\left[-\frac{V}{C^{A1}}\left(t - \frac{\beta w}{FW}\right)\right]\right\} u\left(t - \frac{\beta w}{FW}\right), \tag{13}$$

where $u(t)$ is the Heaviside step function.

If it is only possible to observe marking of terminal species, the observed data will correspond to $w = W$, the effluent state. The corresponding observations are illustrated by Fig. 4.

It is of interest to compare the result given in Eqs. (12) and (13) with that obtained when the same system described by Eq. (10) is studied using a gradientless recirculating reactor, as already treated in detail (*1*). Several important qualitative differences are immediately evident. As seen from Fig. 4, for the plug-flow reactor, there is a delay in the appearance of marked A species at the exit. z^A then immediately reaches its asymptotic value. Such a delay does not occur in the analogous case of the compartmental model, and the appearance of z^A is gradual. Secondly, at the end of the delay period, z^B increases from zero with a positive slope with respect to time in the case of the plug-flow reactor whereas the initial slope for z^B is zero in the case of the gradientless recirculating reactor. Finally, from Eq. (13), we see that z^{A1} and z^B are identical in the case of the plug-flow reactor, contrary to what happens in the gradientless recirculating reactor. Similar differences between plug-flow and gradientless recirculating reactors exist in other cases treated in this paper, but we will not further elaborate these comparisons here.

Two Intermediates

To illustrate the effect of additional steps let us consider the following:

$$A \xrightarrow{V} A1 \xrightarrow{V} B1 \xrightarrow{V} B. \tag{14}$$

Material balance equations over a differential section of the plug-flow reactor become

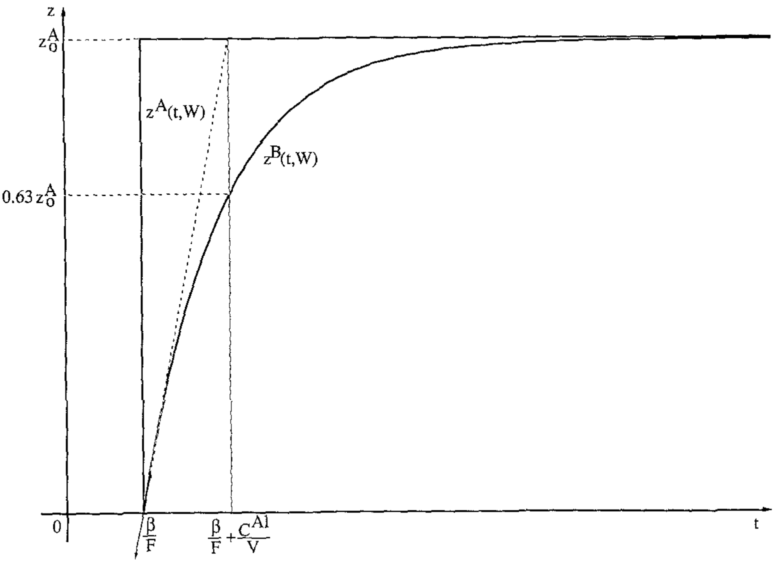

FIG. 4. Observed tracer transients for a model with two unidirectional steps.

$$\frac{\partial}{\partial w}[F^A(w) z^A(t, w)] + \frac{\beta C^A(w)}{W}\frac{\partial}{\partial t} z^A(t, w) = -V z^A(t, w) \quad (15)$$

$$C^{A1}\frac{\partial}{\partial t} z^{A1}(t, w) = V z^A(t, w) - V z^{A1}(t, w) \quad (16)$$

$$C^{B1}\frac{\partial}{\partial t} z^{B1}(t, w) = V z^{A1}(t, w) - V z^{B1}(t, w) \quad (17)$$

$$\frac{\partial}{\partial w}[F^B(w) z^B(t, w)] + \frac{\beta C^B(w)}{W}\frac{\partial}{\partial t} z^B(t, w) = V z^{B1}(t, w). \quad (18)$$

With the same basic assumptions and boundary conditions as previously (with the addition of those for z^{B1}, taken the same as for z^{A1}), provided that $C^{A1} \neq C^{B1}$, we obtain

$$z^B(t, w) = z_0^A \left\{1 + \frac{C^{A1}}{C^{B1} - C^{A1}} \exp\left[-\frac{V}{C^{A1}}\left(t - \frac{\beta w}{FW}\right)\right] + \frac{C^{B1}}{C^{A1} - C^{B1}} \exp\left[-\frac{V}{C^{B1}}\left(t - \frac{\beta w}{FW}\right)\right]\right\} u\left(t - \frac{\beta w}{FW}\right). \quad (19)$$

z^A and z^{A1} are still given by Eqs. (12) and (13), and $z^{B1}(t, w) = z^B(t, w)$. Figure 5 illustrates the observed tracer transients at $w = W$.

When modeling a reaction following Eq. (1), C^{A1} is uniquely identifiable from the knowledge of $z^B(t, W)$. But in the case of of Eq. (14), C^{A1} and C^{B1} are only locally identifiable, since one cannot distinguish between the two time constants C^{A1}/V and C^{B1}/V. The same situation also exists with compartmental modeling of such a system using a gradientless reactor (*9, 10*).

Provided that it can be observed with enough accuracy, the behavior of z^B around $t = \beta/F$ gives useful information about the possible number of intermediates. The slope dz^B/dt just after the delay period is positive in the case of a single intermediate (Fig. 4) but zero in the case of two sequential intermediates (Fig. 5).

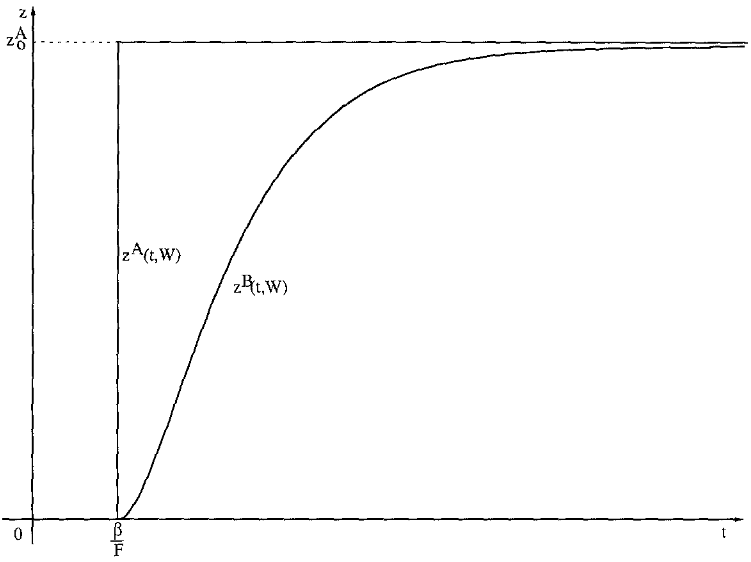

FIG. 5. Observed tracer transients for a model with three unidirectional steps.

Exchange with an Inactive Intermediate

In some cases an intermediate may be converted to an inactive species with which it equilibrates. This condition may be represented as follows:

$$\begin{tikzcd} A \arrow[r, "V"] & A_1 1 \arrow[r, "V"] \arrow[d, shift right, "v_1"'] & B. \\ & A_2 1 \arrow[u, shift right, "v_1"'] & \end{tikzcd} \tag{20}$$

Material balance equations over a differential section of the plug-flow reactor become

$$\frac{\partial}{\partial w}[F^A(w)\,z^A(t,w)] + \frac{\beta C^A(w)}{W}\frac{\partial}{\partial t} z^A(t,w) = -V\,z^A(t,w) \tag{21}$$

$$C^{A_1 1}\frac{\partial}{\partial t} z^{A_1 1}(t,w) = V\,z^A(t,w) - (V+v_1)\,z^{A_1 1}(t,w) + v_1\,z^{A_2 1} \tag{22}$$

$$C^{A_2 1}\frac{\partial}{\partial t} z^{A_2 1}(t,w) = v_1\,z^{A_1 1}(t,w) - v_1\,z^{A_2 1}(t,w) \tag{23}$$

$$\frac{\partial}{\partial w}[F^B(w)\,z^B(t,w)] + \frac{\beta C^B(w)}{W}\frac{\partial}{\partial t} z^B(t,w) = V\,z^{A_1 1}(t,w). \tag{24}$$

The treatment is similar to that of the models described by Eqs. (1) and (14). With the same basic assumptions and similar boundary conditions as used previously, we obtain

$$z^B(t,w) = z_0^A\left[1 + \frac{s_2 + V/C^{A_1 1}}{s_1 - s_2}\exp\left(s_1\left(t - \frac{\beta w}{FW}\right)\right) - \frac{s_1 + V/C^{A_1 1}}{s_1 - s_2}\exp\left(s_2\left(t - \frac{\beta w}{FW}\right)\right)\right] u\left(t - \frac{\beta w}{FW}\right), \tag{25}$$

where s_1 and s_2 are the roots of

$$1 + \left[\frac{C^{A_1 1}}{V} + \frac{C^{A_2 1}}{v_1}\left(1 + \frac{v^1}{V}\right)\right] s + \frac{C^{A_1 1} C^{A_2 1}}{V v_1} s^2 = 0. \tag{26}$$

$z^A(t, w)$ is still given by Eq. (12). Figure 6 illustrates the observed tracer transients.

From Eq. (25) we see that the time constants of the transient part of z^B are $-1/s_1$ and $-1/s_2$. Equation (26) indicates that if v_1 is small enough, or if $C^{A_2 1}$ is big enough, at least one of the time constants will be large. This confirms the intuitive result that z^B will slowly reach its final value if a long-lived

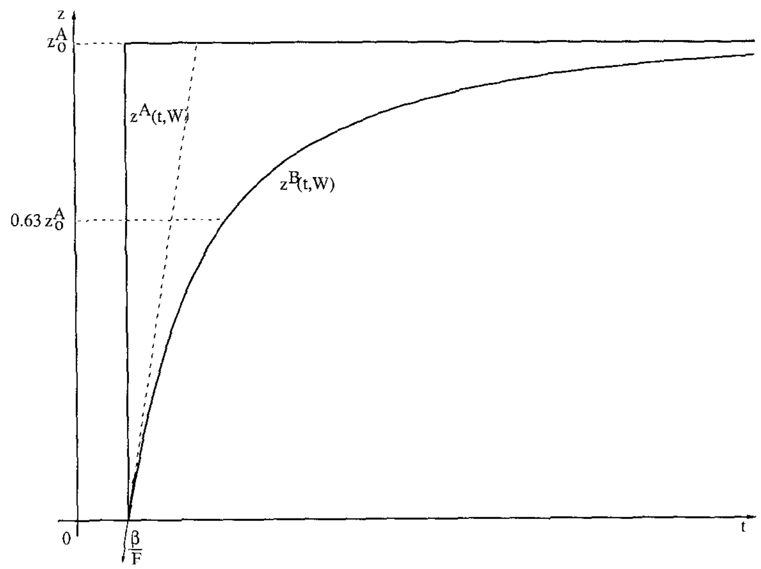

FIG. 6. Observed tracer transients for a model involving exchanges with an inactive intermediate.

intermediate is present that does not lie in the main reaction path.

DISCUSSION

Perhaps the most important pitfall in transient tracing experimentation with plug-flow reactors is the failure to use a proper basic procedure for interpreting the data. Such a procedure must be capable of taking into account the simultaneous transfers of species to, within, and from the catalyst together with the transfers of gaseous species occurring along the catalyst bed. A natural framework for the construction of models, presented in this paper, is obtained through the use of the appropriate differential equations. Such a procedure, to our knowledge, has not been used in studies reported in the literature.

For example, recent studies by Biloen and co-workers (*5*, *6*), with plug-flow transient tracing by ^{13}CO, use compartmental models for describing what takes place at the surface of the catalyst in terms of interconnected pools (or compartments). A more elaborate pool model has also been employed in a study by de Pontes *et al.* (*7*), also using a plug-flow reactor. It might be of interest to apply the formalism presented here to the type of data obtained in plug-flow reactors, rather than using a compartmental model formalism suited to the interpretation of data obtained in gradientless recirculating reactors.

APPENDIX 1: NOMENCLATURE (TYPICAL UNITS)

A	reaction component
$A1$, $B1$, A_11, A_21	adsorbed intermediates
B	reaction component
C^A, C^B	concentration of A and B in gas phase, volume fraction
C^X	concentration of intermediate X, where $X = A1, B1, A_11$, or A_21, on catalyst surface per unit mass of catalyst, ml STP/g
$F^A(w)$, $F^B(w)$	flow rate A and B at axial position w in bed, ml STP/(s · g)
F	initial flow rate of A at $w = 0$ ($F = F^A(w) + F^B(w)$), ml STP/(s · g)
t	time, s

$u(t-k)$	unit step function (Heaviside step) with value of 0 at $t < k$ and unity at $t \geq k$
$v_1, v_{\pm 1}, v_{\pm 2}$	reaction rate of individual steps per unit mass of catalyst, ml STP/(s · g)
V	overall reaction rate per unit mass of catalyst, ml STP/(s · g)
w	axial position in bed, expressed as the mass of catalyst traversed from inlet, g
W	total mass of catalyst bed, g
z_0^A	fraction of traced A in the feed for $t \geq 0$
$z^i(t, w)$	fractional tracer marking in circulating stream of product i as variant with time and space; $i = A, A1, B1, A_11, A_21, B$
β	dead space including voids in catalyst bed (for a recirculating reactor it also includes space outside the catalyst bed proper), ml STP

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REFERENCES

1. Happel, J., "Isotopic Assessment of Heterogeneous Catalysis." Academic Press, Orlando, FL, 1986.
2. Froment, G. F., and Bischoff, K. B., "Chemical Reactor Analysis and Design." Wiley, New York, 1979.
3. Godfrey, K., "Compartmental Models and their Application." Academic Press, London, 1983.
4. Happel, J., Walter, E., and Lecourtier, Y., *I&EC Fundam.* **25,** 704 (1986).
5. Soong, Y., Krishna, K., and Biloen, P., *J. Catal.* **97,** 330 (1986).
6. Zhang, X., and Biloen, P., *J. Catal.* **98,** 468 (1986).
7. de Pontes, M., Yokomizo, G. H., and Bell, A. T., *J. Catal.* **104,** 147 (1987).
8. Winslow, P., and Bell, A. T., *J. Catal.* **91,** 142 (1985).
9. Walter, E., Lecourtier, Y., Happel, J., and Kao, R. J.-Y., *AIChE J.* **32,** 1360 (1986).
10. Walter, E., Ed., "Identifiability of Parametric Models." Pergamon, Oxford, 1987.