Tracer Experiments and RTD's in Heterogeneous Reactor Analysis and Design

This paper focuses on the problem of scale-up of two-phase (e.g., solid-fluid) reactors. It outlines a class of such reactors which, for first-order reactions, scale in the familiar single-phase manner via an analog of the usual residence time distribution formula. The differences lie in the fact that the appropriate tracer experiment entering the formalism for this reactor class refers to a nonadsorbing tracer, and the analog of the plug flow solution is the solution for a fixed bed with fluid-phase plug flow. Surprisingly, unlike single-phase systems, there exist two-phase reactors, outside of the class defined, that do not scale in this manner, even when, say, the true catalyst surface chemistry is purely first-order. The paper discusses a few examples and implications for the design of two-phase reactors, including fluidized beds.

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Introduction

Since their introduction into chemical engineering, residence time distribution functions have become invaluable tools for design, analysis and scale-up of single-phase, isothermal chemical reactors with premixed feeds. A residence time flow description enables one to predict exact reactor performance when the chemistry is exclusively first-order reactions and to bound its performance when the chemistry is a single *n*th-order reaction (Zwietering, 1959).

The majority of chemical reactors, including almost all (even homogeneous) catalytic reactors, are multiphase. It is often assumed that the general notions of residence time distributions carry over to heterogeneous reactors. Figure 1 (Biloen et al., 1983), the response in the effluent of a fixed bed, Fisher-Tropsh synthesis over nickel reactor to step inputs of He and of $C^{13}O$, illustrates that the notion of residence times is much more complex in multiphase systems. Helium, which does not adsorb onto the catalyst, exhibits a plug-flow residence time distribution (RTD) curve characterizing the reactor's fluid flow. Each of $C^{13}O$, $C^{13}H_4$, $C^{13}_3H_6$, and He, however, exhibits a different residence time distribution within the reactor, because each species has a different solid-fluid exchange rate. As in most multiphase reactors, the total residence time is species-dependent. Thus, the reactions couple to the residence time of an entering molecule, thereby depriving the residence time of its original meaning. Species-dependent diffusion, in principle, causes similar effects in single-phase reactors, but usually of negligible importance; a single-phase, species-independent residence time distribution is usually a very good assumption.

In this paper, we investigate the applicability of tracer experiments and residence time distributions to predict the performance of heterogeneous reactors. We do not concern ourselves with the use of nonreacting tracers to detect reactor flow maldistributions, a topic already treated in the literature (Shinnar, 1987), but rather with predicting the outcome of first-order reactions. We argue that, although true residence time distributions do not make much sense in heterogeneous reactors, there does exist a related notion that, under certain circumstances, plays an analogous role. The analysis sheds some light on important scale-up problems in heterogeneous reactors.

Assumptions

We consider reactors comprised of one "inner" (fluid) phase and one "outer" (solid catalyst or adsorbed) phase. The outer phase does not participate in the feed or the effluent, but all reactions take place there. A typical scenario is: reactant enters the feed (in the inner phase), makes one or more excursions into the outer phase where it may or may not react, and eventually leaves the reactor after having returned to the inner phase. For catalyst pellets, one can define the boundary of the outer phase as, say, the exterior pellet surface and the inner phase as the fluid between particles. Alternately, one can include the macropores (where diffusion is still species-independent) as part of the inner phase. We consider only isothermal reactors whose fluid mechanics are at steady state and whose (outer phase) chemistry is a network of reversible first-order reactions. Since particle number is conserved, one may speak of excursions of "a molecule" to the outer phase whether or not the molecule reacts.

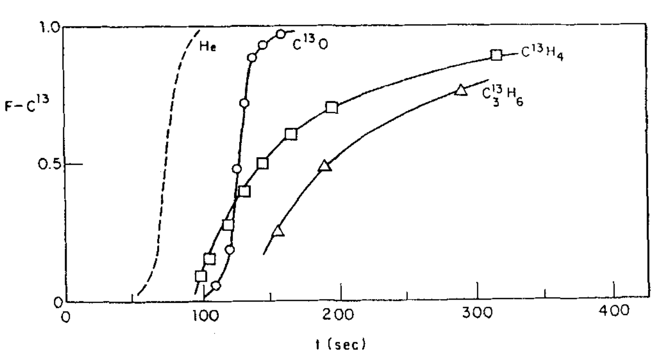

Figure 1. Response (cumulative distribution function) of a packed-bed Fisher Tropsh reactor to a step input of C^{13}O and He.

Figure shows that the residence time in the reactor and in the reactive phase is species dependent. From Biolen et al. (1983).

The conventional approach to packed-bed and Berty (mixed) reactors lumps all transport and diffusion processes inside the solid particle, adsorption, desorption, and first-order reaction into a phenomenological set of apparent homogeneous, first-order reactions. The apparent rate constants are typically expressed in units of [(weight or moles)/weight catalyst]/time. One then invokes the usual single-phase design formalism to obtain: the outlet concentration c_j^{out} of species j $(1 \leq j \leq N)$ in terms of the Laplace transform of the residence time distribution $f_o(t)$ of an exclusively inner-phase (i.e., nonadsorbing) tracer; the $\{\lambda_k\}$ of eigenvalue of the apparent rate constant matrix; and coefficients $\{a_{kj}\}$ depending on this matrix and on the inlet conditions. For, say, an apparent rate constant matrix, corresponding to a set of reactions that are detailed balanced at equilibrium, one has:

$$c_j^{\text{out}} = \int_0^\infty f_o(t) c_{j,\text{plug}}^{\text{out}}(t)\,dt = a_{0j} + \sum_{k-1}^{N-1} a_{kj} \hat{f}_o(-\lambda_k). \qquad (1)$$

For example, Wei and Prater (1962) assume inner-phase plug flow or $\hat{f}_o(-\lambda_k) = e^{\lambda_k \tau_o}$, which we have dedimensionalized by multiplying by the mean τ_o of $f_o(t)$. This τ_o is not related to a tracer study using an isotope of a reaction participant. The quantity τ_p usually reported is the product of τ_o with the ratio of the packing-dependent apparent catalyst density (weight catalyst/volume reactor) to the molar or mass fluid density. This packing dependence and the dependence on fluid density and reactor conditions make *a priori* predictions based on τ_o difficult. Therefore, rate data are usually reported in terms of τ_p.

It is well known that one can use $f_o(t)$ to assess the effects of flow maldistributions. We shall derive Eq. 1 and thereby show when one can use $f_o(t)$ to predict reactor performance as well.

This paper, like Shinnar et al. (1971) in another context, considers only reactors satisfying:

Assumption 1. The distribution of times spent by molecules of every species in the inner phase only while traversing the reactor—irrespective of the times spent in the outer phase—is the same as $f_o(t)$.

Assumption 2. The chance that a molecule will change phases depends only on the molecule's current state (i.e., its species and in which phase it resides), not upon its history, environment, or position in the reactor.

Assumption 1 requires outer-phase motion to be such that excursions into the outer phase (and, possibly, reaction there) do not affect the amount of time spent by molecules in the inner phase and thus that inner-phase transport be species-independent. Basically, this time must be the same as the time spent in the system by a molecule that is unable to visit the outer phase. Assumption 2 demands that the catalyst properties be uniform, the system have no memory and inter-phase transport be first-order, i.e., Markoff. It requires the width of the interstitial channels (between catalyst particles, for example) to be such that diffusion or mixing normal to the local direction of flow in those channels is fast compared with inter-phase transport times.

One would normally measure $f_o(t)$ with a tracer that does not leave the inner phase. Since it is usually difficult to find a tracer that does not enter at least the macropores, it is worth mentioning when one can include them in the inner phase. For this to be permitted it is necessary to ensure that there is no macropore diffusion resistance and that film mass transfer resistance external to the particles is not controlling. Otherwise, the fluid-solid interphase transport coefficient h_i for species i, say, would depend on local velocity and thereby violate assumption 2. This type of problem occurs more frequently in pilot plants than in industrial reactors.

What kind of phase (e.g., solid-fluid) contacting satisfies the first assumption? Imprecisely, the inner-phase flow divides the reactor into sets of mutually equivalent points characterized by nonadsorbing molecules at those points having common inner-phase ages. A reactor satisfies assumption 1 if the outer-phase motion is such that every infinitesimal element of outer phase remains for all times within or differentially close to the set of equivalent positions in which it began. We bypass this technical discussion and resort here to example.

Consider a fixed-bed reactor where the characteristic solid particle (outer phase) size is much smaller than the reactor diameter. After an excursion into the outer phase (i.e., adsorption and possibly reaction), a molecule returns to the inner phase at approximately the same position from which it departed to continue its inner-phase trip as if it had never left. For smooth inner-phase motion, assumption 1 should hold.

Arbitrary motion of the outer phase, on the other hand, may severely alter the molecule's journey through the inner phase (and thereby violate our assumptions) by, for example, depositing near the reactor outlet a molecule that entered the outer phase near the reactor inlet. All cases where the solid phase moves, however, need not violate assumption 1. For example, when the inner phase is in plug flow, return of a molecule to the inner phase at the same axial position from which it departed (as accomplished by purely transverse outer-phase mixing) does not affect the validity of the assumptions. That is, for inner-phase plug flow, points along the same cross sections have the same inner-phase ages and thus are equivalent.

Consider now a perfectly-mixed inner phase. No matter where in the inner phase a molecule returns, it will be arbitrarily close to points with every possible inner phase age and every possible future life, including points with the same inner-phase age as the molecule had prior to visiting the outer phase. Thus, irrespective of outer phase motion, assumption 1 remains in force.

The Argument

In this section, we argue that the description of the processes of transport from the inner to the outer phase, reaction in the outer phase and transport back to the inner phase, together, takes equations identical with those for a (possibly different) set of first-order reactions solely among inner-phase species and independent of additional details of the mixing. This result is similar in spirit to Wei's (1962) extension of the Thiele-Zeldovitch problem. He shows that diffusion into a catalyst followed by a set of true isothermal first-order reactions and diffusive exit from the catalyst has a reduced description as an apparent set of first-order reactions. As in his case, our apparent set of first-order reactions may differ from the true set of outer-phase reactions. For example, series outer-phase reactions can appear as parallel apparent reactions.

Let us adopt a probabilistic view, i.e., in terms of Markoff process (Feller, 1968), of first-order interphase transport and first-order reactions. Each species in each phase corresponds to one state (N-inner and M-outer states, where M may be much larger than N) in the Markoff analogy. Since particle number is conserved in the system, the probability at any time that corresponds to a state is just the fraction of molecules in that state. The reactions and the interphase transport processes represent the allowable transitions between states, where the rate constants and interphase transport coefficients are the short-time probabilities/time for these transitions. Shinnar et al. (1973) show that with the concentrations normalized to sum to one, the transport-reaction equations of this physical system are identical to the Kolmogorov forward equations for the Markoff process just described. We argue that at steady state these reduce to a set of apparent transition probabilities $\{k_{ji}:i, j = 1, \ldots, N$ with $i \neq j\}$ among the N states corresponding to the inner-phase species only, even though in the full description the only allowed transition from inner-phase state i is $i \rightarrow i*$, where the $*$ denotes the corresponding outer-phase species. These apparent probabilities generate a reduced Markoff process which we interpret as an apparent set of inner-phase first-order reactions.

We employ the following facts, proved in the Supplementary Material, that depend only on the linearity of the processes, irrespective of whether or not the reactor's chemistry is at steady state: every particle entering an outer state ultimately returns to an inner state; a particle initially in state i either remains i or takes a trip to the outer phase and eventually returns to the inner phase in state j (or i again). One may then speak of a conditional "trip" probability $p_{j:i*}$ ($p_{i:i*}$) (given explicitly in the Supplementary Material) that the inner-phase state to which the molecule eventually returns is state $j(i)$, given that it entered the outer phase from state i. This probability depends only on the two subscripted states and on the transition probabilities of the true description; it does not depend on the population of any starred state. By assumption 2, it is uniform throughout the reactor.

Particles in inner-phase state i with inner-phase age τ jump to outer phase state $i*$ at a rate given by the transition probability/time h_i. Since the system is at steady state, there is no accumulation of such particles in the outer phase. So, they are replaced at the same rate in the inner phase by particles that left the inner phase from state i with the same inner-phase age τ some time earlier. These particles return, by hypothesis, to points in the reactor characterized by the fluid flow as having inner-phase ages τ, and they return in state j with probability $p_{j:i*}$. Thus, the apparent probability k_{ji} of a particle leaving state i and a particle simultaneously entering state j, apparently a jump from state i to j, is

$$k_{ji} = h_i p_{j:i*}. \tag{2a}$$

The apparent probability of no jump is

$$= 1 - (h_1 + \ldots + h_N) + h_i p_{i:i*}. \tag{2b}$$

The $\{k_{ij}:i, j = 1, \ldots, N$ with $i \neq j\}$ generates a reduced Markoff process, the equivalent of a set of first-order reactions among only the N inner-phase species.

By assumption 2, this reduced description is uniform throughout the reactor; by assumption 1 inner-phase transport is species-independent. Consequently, the reactor behaves as if it were a single-phase reactor with residence time distribution $f_o(\tau)$ of the inner phase of the true reactor, in which the apparent set of first-order reactions occurs. Since the conditional probability is dimensionless, the rate constants (Eq. 2a) inherit units (inverse to those of the inner-phase residence times) from the $\{h_i:i = 1, \ldots, N\}$. Standard single-phase scaling of steady-state first-order reactions predicts the effluent of a design reactor by integrating the steady-state performance of an inner-phase plug flow (i.e., packed-bed) reactor having residence time τ_o against the design reactor's $f_o(\tau_o)$; this leads to Eq. 1. Since both Berty and packed-bed reactors satisfy our second section's assumptions, the reduced description for a given reaction system will be the same for both. Thus, one can use parameters obtained from experiments done on one to design and scale the other.

Inner-phase residence time, called "crazy clock" time by D. Prater, is clearly not the real time spent by any reaction participant in the reactor. Therefore, steady-state reaction rate measurements, which are necessarily based on the crazy clock, will not predict the reactor's dynamic behavior and cannot be used for control purposes.

The reduced description does lend itself to the analysis of a reactor's chemical dynamics when the reactor's fluid mechanics are at steady state. Although we leave the mathematical arguments for a future article, we note that under appropriate conditions including the hypotheses of the Assumptions section, one can express the Laplace transform $\hat{c}_j^{\text{out}}(s)$ of the dynamics of the reactor's outlet concentration $c_j^{\text{out}}(t)$ of species j by

$$\hat{c}_j^{\text{out}}(s) = \int_0^\infty [\hat{c}_{j,\text{fixed bed}}^{\text{out}}(s, \tau)] f_o(\tau) d\tau. \tag{3}$$

As illustrated in the Examples section, the fixed-bed solution contains the usual sum of terms, each of which is a coefficient multiplied by the corresponding relevant eigenvector. Each coefficient will involve the usual term deriving from the feed concentration (which survives in the steady-state limit) and a term that depends on the initial condition (at $t = 0$) of c and of c^*. The latter term will disappear at steady state. The operator whose spectrum appears in this solution has a number of interesting properties upon which we comment in the Examples section.

Before discussing design implications, we note that, in addition to the first-order outer-phase reactions, one may allow first-order inner-phase reactions by replacing Eq. 2a with

$$k_{ji} = h_i p_{j:i*} + k'_{ji}. \tag{2a'}$$

Here k'_{ji} is the rate constant for the inner phase reaction $i \rightarrow j$ without excursion into the outer phase. One can also allow (inductively) a finite number of outer phases.

Implications for Reactor Design and Scale-Up

Before proceeding we must address the issue of relevance: there are almost no truly first-order reactions. There are, however, many systems that, within their range of operation, approximate first-order systems. The most common are nonlinear reactions where all but one reactant is present in excess. In addition, reactions having Langmuir-Hinshelwood- or Ely-Rideal-type kinetics often operate in a concentration region where the denominator in the rate expression is dominated by the constant term or by the concentrations of species that remain fairly constant with time.

The major utility of residence time distributions in homogeneous reactors is to detect flow maldistributions in operating reactors and to aid in understanding the problems faced in design and scale-up. Only then, do they sometimes allow the translation of a careful tracer experiment to performance predictions. Although there exist distributions analogous to residence time distributions for the heterogeneous reactors described above, not only do the usual cautions apply but even the choice of tracer is a delicate matter. Whereas an isotope of a reactant may appear to be the ("proper") tracer that gives the best picture of what is happening in the reactor, the resulting distribution may not necessarily be directly applicable to scaling. For this we have seen that a nonadsorbing tracer is more useful.

Let us point out some potential problems, say in, a packed bed that one must eliminate before scaling. Although most packed-bed reactors operate with the fluid in nearly plug flow, pilot-size reactors sometimes have a length-to-diameter ratio (and hence pressure drop) too low to preclude maldistributions. An inert tracer that does not diffuse into the particles at all is the best means to check for this. In addition, a pilot reactor that is too small and that has insufficient fluid velocity can provide distorted kinetics by allowing heat of reaction effects (e.g., internal temperature gradients) to couple to reaction. Exotic dynamics found in a pilot reactor that derive from this coupling may disappear in a large reactor which has higher flow rates. Silverstein and Shinnar (1982) discuss how one can test for this with an inert tracer having fluid phase and macropore diffusion properties similar to those of the reactants.

Fluidized beds have several features that violate our assumptions. The solid catalyst moves and carries adsorbed species with it, probably violating our first assumption. Moreover, the time scale of this motion can change with scale-up. In addition, since particles tend to aggregate and leave more and less "dense" (mass of solids per unit volume reactor) regions, the chance of a particle changing phases depends upon its position (i.e., the local "density" it sees) in the reactor. The latter effect is most pronounced in bubbling beds but is also true in turbulent beds. Catalyst-particle-size distribution strongly affects this "density" variation, which itself may vary temporally during operation. Although the addition of sufficient "fines" to a turbulent bed usually remedies "density" variation, one must still exercise caution in scaling fluidized beds.

How does one determine if the solid motion in a fluidized bed violates the assumptions previously mentioned? Recall that Shinnar et al. (1972) compare the responses at the reactor outlet of a nonadsorbing tracer and an adsorbing tracer for a reactor that satisfies assumptions 1 and 2. When the adsorbing tracer's interphase exchange is very fast relative to the time scales of fluid flow, they show that the two responses have the same functional form, but the adsorbing tracer's response is stretched, i.e., it has a larger mean. This result is quite intuitive. Adherence to assumption 1 returns a molecule to the same inner phase locality from which it embarked on its sojourn to the outer phase. Fast interphase transport ensures that a molecule changes phases so often and quickly that the amount of time it spends locally in the inner phase is a fixed, uniform fraction (determined from the equilibrium partition coefficient) of the total time that it spends locally in both phases. Uniformity of this partition coefficient then preserves the form of the response but stretches it by a similar factor. Compare, for example, the curves for He and $C^{13}O$ in Figure 1 with $C^{13}O$ the quickly adsorbing tracer. On the other hand, lack of interphase exchange equilibrium (as in the other curves in Figure 1), smears the response of the adsorbing species.

Violation of assumption 1 will also result in a change in the form of the response of the adsorbing tracer, because trips to the outer phase return molecules to new inner phase localities. Moreover, the larger the (equilibrium) holdup of this tracer the more disparate will be the responses of the two tracers even for arbitrarily fast interphase exchange rates. This result is also intuitive. Consider, by analogy, two very long trains moving with equal speeds, but in opposite directions. Consider a passenger walking towards the front of one of the trains who, in the course of walking forward a few meters, always jumps between the two trains many times. Since neither train is stationary relative to a reference frame fixed to the earth, interjumping violates assumption 1. Arbitrary increase of the jumping rate only makes the fraction of time spent on each of the trains uniform for his entire walk. The passenger's net forward motion will then depend simply on the fraction of time that he spends on each of the two trains. The higher the holdup or the larger the fraction of time that the passenger spends on the train that is moving backwards, the less similar the passenger's progress will be to that of someone who walks at the same speed without ever jumping between trains.

Thus, by analogy, in order to check assumptions 1 and 2 experimentally, one will need two tracers, one nonadsorbing tracer and one strongly adsorbing tracer (i.e., with a high outer-phase holdup) that adsorbs and desorbs quickly (relative to fluid flow time scales). In order to test if the strongly adsorbing tracer's interphase transport is fast enough, one should run both of these tracers simultaneously through a packed-bed reactor, a reactor that we know satisfies assumptions 1 and 2. If the two responses are similar in form, yet differ in scale, then the adsorbing tracer's interphase exchange rate is fast enough. Then, one should run the same dual-tracer experiment on the fluidized bed in question. Only if the two tracer responses are again similar in form and differ only by a stretch factor can one expect our assumptions to hold for the fluidized bed. This test is the easiest and most convincing, and hence scale-up is the safest when the fluid flow is close to plug flow or to a series of stirred tanks.

For turbulent beds with sufficient "fines" that fail this test, it is still possible to mediate the degree to which the reactor violates our assumptions. One can change the catalyst-size distribution (cf. assumption 2) and modify the reactor's design by restricting or compartmentalizing the solid's vertical backmixing with baffles. For example, when the fluid flow is plug-like, purely transverse solid mixing respects the hypotheses of assumptions 1 and 2. This is exactly what horizontal (i.e., normal to flow) baffles accomplish. They localize solid backmixing

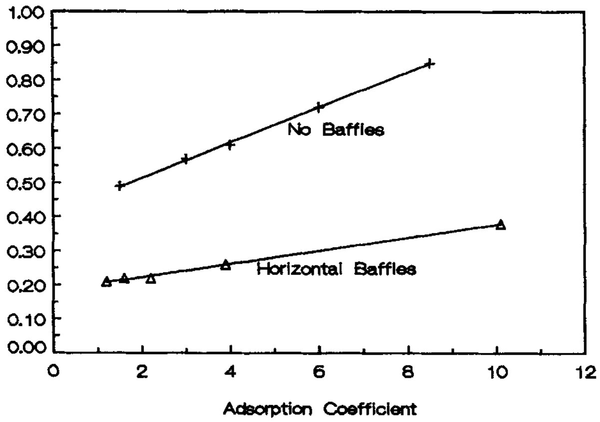

Figure 2. A comparison of the square of the standard deviations of pulse tracer response curves.

Standard deviations are normalized with the tracer's mean residence time. Response curves are for one reactor with no baffles and one with horizontal (normal to the directions of overall fluid flow) baffles.

Adapted from Krambeck et al. (1987) and Avidan et al. (1986).

basically to cross sections and force the fluid to proceed in a plug-like fashion. As a bonus, they prevent fluid regions from having prolonged periods with minimal catalyst contact. It is such a design that we feel allows fairly confident scale-up.

Figure 2, made from data presented in Krambeck et al. (1987) and Avidan et al. (1986) support these conclusions. For a zeolite catalyst, Krambeck et al. use the tracer sulfur hexafluoride. This tracer has the fascinating property that it adsorbs and desorbs very quickly, yet varying the humidity can radically shift its equilibrium adsorbed holdup. By seeing how small the normalized variance of the tracer's response is, i.e., how closely it resembles bypass-free plug flow, Krambeck et al. showed (cf., Figure 2) that the introduction of horizontal baffles into a fluidized bed dramatically reduced both the actual variances as well as their difference for the extreme cases of low and high humidity. Thus horizontal baffles work to bring both the high- and low-humidity responses into the same (plug-flow like) functional form, as required for safe scale-up.

It has also been suggested (Nauman and Collinge, 1968; Nauman and Buffham, 1983) that one could use the response of the adsorbing tracer as a basis for design and scale-up. Since solid-mixing nonuniformities that violate our assumptions may not scale reliably when the responses of an adsorbing and a nonadsorbing tracer differ in form, such predictions may sometimes be misleading.

Another way to study the lateral nonuniformities is to observe the effect of temperature in a packed-bed reactor on the performance of a catalytic reaction whose kinetics are known (Glasser et al., 1973; Naumann and Collinge, 1968). The Laplace-transform of the so-called *contact time distribution* so obtained is useful for understanding flow maldistributions in industrial reactors and in predicting other packed-bed performance. In a fluidized bed, however, the way that the contact time distribution will vary as the catalyst moves will depend on the specific reactants and reactions. It may not be valid for another reaction, even over the same catalyst.

For nonfirst-order surface reactions it is not at all clear that one may scale between a fixed bed and a Berty reactor, yet experience tells us that it does frequently work. In practice, one would compare experiments on small fixed bed and Berty reactors to see if the latter's performance is conceivably some average of fixed-bed performances. If this is successful, one may say that the reaction is "weakly nonlinear" and one can try to use the fixed-bed data to scale cautiously to a larger reactor. The predicted yields will certainly be off, but most likely by acceptable percentages.

If this averaging procedure is not successful, then the reaction is probably either autocatalytic or otherwise strongly nonlinear and residence time distributions are of no use in scaling. One should carefully scale such reactions only to reactors that resemble as closely as possible a clearly defined (in terms of its micro- as well as its macromixing) ideal reactor such as a Berty reactor, a series of Berty reactors, or a fixed bed.

Examples

We consider three examples, two that satisfy our assumptions and a third which does not, all of which deal with the following system.

Consider a chemical system with N inner-phase and $M = N$ outer-phase species and with first-order outer-phase reactions, as described above. Suppose that the two phases are sufficiently intermingled that, over the length scales of interest, every volume element within the reactor has a ratio of solid-to-void volume given by α, where α is uniform throughout the reactor. Molecules of each of the N inner-phase species can transfer (a Markoff process) between phases.

Let $V = \mathbb{R}^N$ be an N-dimensional, real, linear vector space whose N natural basis vectors correspond in the natural way to the N species. That is, if $c \epsilon V$ is the inner-phase concentration vector, then the component c_i of c along the ith natural basis vector $e^i := (0, \ldots, 0, 1, 0, \ldots 0)^t$ (the 1 is in the ith position) is the concentration of the ith species in the inner phase. For any $x \epsilon V$, let diag x be the $N \times N$ diagonal matrix:

$$(\mathrm{diag}\, x)_{ij} = x_i \delta_{ij}. \tag{4}$$

Let $c^* \epsilon V$ be the vector of outer-phase concentrations. One may form the usual rate constant matrix $A^*: V \longrightarrow V$:

$$A^*_{ij} \begin{cases} = k^*_{ij}, & \text{if } j^* \longrightarrow i^* \text{ is a reaction} \\ = 0, & \text{if } i \neq j \text{ and if } j^* \longrightarrow i^* \text{ is not a reaction} \\ = -\sum\limits_{m:m \neq j} k^*_{mj}, & \text{if } i = j, \end{cases} \tag{5}$$

where $k^*_{ij} > 0$ is the rate constant for the reaction $j^* \longrightarrow i^*$. In this example, we presume that the set of reactions is reversible and is detailed balanced at equilibrium. This is equivalent to assuming that there exists a vector $c^e \epsilon V$ determined up to positive scalar multiple, whose components are all positive such that A^* diag c^e is symmetric. For simplicity, we presume there are no other nonnegative equilibria.

Since the interphase transport is Markoff, for each species i there exist positive numbers h_i and h_i^* such that the local transfer rate of species i from the inner to the outer phase and from the outer to the inner phase is given by $h_i c_i$ and $h_i^* c_i^*$, respectively. We choose the units of the interphase transport coefficients h_i and h_i^* such that both $h_i c_i$ and $h_i^* c_i^*$ have units of moles i per unit fluid volume per unit time.

Consider the processes described above occurring in three types of ideal, two-phase reactors. We presume that one can adequately model each phase of each reactor by an ideal flow model (uniformity in the directions normal to flow and either complete or zero mixing in the direction of flow) and that the reactors have uniform cross sections. All reactors are at steady stage.

First consider a fixed-bed reactor whose inner (fluid) phase is in plug flow. Both $\boldsymbol{c}$ and $\boldsymbol{c}^*$ are functions of $z (0 \le z \le L)$, the coordinate along the direction of flow. One begins with local (in z) steady-state balances for each species in each phase and manipulates them into the form

$$\frac{d\boldsymbol{c}(z)}{dz} = (\alpha\tau_o/L)[\boldsymbol{A}^*(\text{diag}\,\boldsymbol{h}^* - \alpha\boldsymbol{A}^*)^{-1}\ \text{diag}\,\boldsymbol{h}]\boldsymbol{c}(z). \quad (6)$$

The solution of Eq. 6 is

$$\boldsymbol{c}(z) - \boldsymbol{c}^e = \sum_{k=1}^{n-1} \boldsymbol{x}^k \cdot \{[(\text{diag}\,\boldsymbol{h})(\text{diag}\,\boldsymbol{c}^e)^{-1}(\text{diag}\,\boldsymbol{h}^*/\alpha)^{-1}]\boldsymbol{c}^f \cdot \boldsymbol{x}^k\} e^{\alpha\tau_o(z/L)\omega_k}. \quad (7)$$

In Eq. 7, $\boldsymbol{x}^k$ and ω_k are the kth eigenvector and eigenvalue of the matrix in the square brackets in Eq. 6, $\boldsymbol{c}^f$ is the feed concentration and the equilibrium vector $\boldsymbol{c}^e$ is proportional to the positive eigenvector $\boldsymbol{x}^0$ corresponding to $\omega_0 = 0$. This matrix has all of the properties normally associated with a rate constant matrix for a first-order reaction system. Of importance here is: When $\boldsymbol{A}^*$ is detailed, balanced at equilibrium ω_k is real and negative for all $k = 1, \ldots, N - 1$.

In a Berty reactor, both phases are well mixed; thus, neither $\boldsymbol{c}$ nor $\boldsymbol{c}^*$ depends on z. Beginning with a global species balance for each species in each phase and rearranging, one arrives at

$$\boldsymbol{c} - \boldsymbol{c}^f = \alpha\tau_o\,[\boldsymbol{A}^*(\text{diag}\,\boldsymbol{h}^* - \alpha\boldsymbol{A}^*)^{-1}\,\text{diag}\,\boldsymbol{h}]\boldsymbol{c}. \quad (8)$$

The solution to Eq. 8 is

$$\boldsymbol{c} - \boldsymbol{c}^e = \sum_{k=1}^{n-1} \boldsymbol{x}^k\{[(\text{diag}\,\boldsymbol{h})(\text{diag}\,\boldsymbol{c}^e)^{-1}(\text{diag}\,\boldsymbol{h}^*/\alpha)^{-1}]\boldsymbol{c}^f \cdot \boldsymbol{x}^k\}(1 - \alpha\tau_o\omega_k)^{-1}. \quad (9)$$

Note that Eqs. 7 and 9 take the steady-state form prescribed by Eq. 1. In the previous section we argued that, subject to assumptions 1 and 2, adsorption, first-order reaction and desorption, together, expressed themselves as an apparent set of first-order reactions, independent of the details of phase contacting pattern beyond our assumptions. Consequently, the single-phase, first-order scale-up procedure should apply, with $f_o(\tau)$ the appropriate residence time distribution. This is born out in the above example. The fact that the same matrix appears on the right sides of Eqs. 6 and 8 and that it has the properties of a first-order rate constant matrix illustrates the first conclusion. To demonstrate the latter note that f_o for the fixed bed and the Berty reactors are $\delta(t - \tau_o)$ and $(1/\tau_o)e^{-t/\tau_o}$, respectively, and that

$$(\boldsymbol{c} - \boldsymbol{c}^e)_{\text{Berty}} = \int_0^\infty (\boldsymbol{c}(z = L_{jt}) - \boldsymbol{c}^e)_{\text{Fixed Bed}}\, f_o(t)_{\text{Berty}}\, dt, \quad (10)$$

which one can easily verify from Eqs. 7 and 9. In Eq. 10, $\boldsymbol{c}(z, t)$ is $\boldsymbol{c}(z)$ of Eq. 7 with t replacing τ_o.

Consider now an example which violates assumptions 1 and 2, a reactor whose fluid phase is in plug flow and whose solid phase is well mixed. Here, $\boldsymbol{c}$ is a function of z while $\boldsymbol{c}^*$ is not. The solution of the rearranged balance equations is

$$\boldsymbol{c}(z) = \sum_{k=0}^{N-1} [(\text{diag}\,\boldsymbol{c}^e)^{-1}(\text{diag}\,\boldsymbol{h}^*)^{-1}(\text{diag}\,\boldsymbol{h})[\boldsymbol{I} - e^{-\tau_o \text{diag}\,\boldsymbol{h}}] \cdot [\boldsymbol{I} - e^{-\tau_o(z/L)\,\text{diag}\,\boldsymbol{h}}]^{-1}\boldsymbol{y}^k(\tau_o) \cdot \boldsymbol{c}^f]\theta_k(\tau_o)\boldsymbol{y}^k(\tau_o). \quad (11)$$

In Eq. 11, $\boldsymbol{y}^k(\tau_o)$ and $\theta_k(\tau_o)$ and the kth eigenvector and eigenvalue of a matrix whose elements depend on τ_o and where $e^{\boldsymbol{B}}$ for some diagonal matrix $\boldsymbol{B}$ is just the diagonal matrix with

$$(e^{\boldsymbol{B}})_{ij} = e^{(B_{ij})}.$$

Equation 11 is not related to Eq. 7 via a transformation like Eq. 10, except in some limiting cases. In particular, the Argument section's scaling of fixed-bed data to this type of reactor is not valid. Any attempt to do so could result in serious error. Figure 3 gives a simple numerical illustration of the difference between the three types of reactors described above for the reaction mechanism $A_1 \rightleftharpoons A_2 \rightleftharpoons A_3 \rightleftharpoons A_4$. The parameters used in the calculation are $N = M = 4$, $\alpha = 1$, $\tau_o = 10$, $\boldsymbol{c}^f = (1, 0, 0, 0)'$, $\boldsymbol{h} = (1, 10, 1, 1)'$, and $\boldsymbol{h}^* = (1, 1, 1, 1)'$; rate constant equals 1 for all forward reactions and rate constant equals 0.01 for all reverse reactions. These differences can be quite significant.

Before concluding this section we illustrate the result (Eq. 3) for Laplace transformed dynamics in the context of the example worked in this section. This formula gave the Laplace transform of the reactor's time varying effluent concentration as an integral over $f_o(\tau)$ of a fixed-bed solution. Let $\boldsymbol{c}_o$ and $\boldsymbol{c}_o^*$ be the $t = 0$ concentrations in the inner and outer phases, respectively, let $\boldsymbol{Z} = [(\text{diag}\,\boldsymbol{h}^*)(\text{diag}\ \boldsymbol{c}^e)(\text{diag}\,\boldsymbol{h})^{-1}]^{1/2}$, $\boldsymbol{R}(s) = \{(\alpha\boldsymbol{A}^* - s\boldsymbol{I})(s\boldsymbol{I} + \text{diag}\,\boldsymbol{h}^* - \alpha\boldsymbol{A}^*)^{-1}\}\ \text{diag}\ \boldsymbol{h}$ and let $\{\boldsymbol{x}^j(s), \omega_j(s): j = 1, \ldots, N\}$ be the s-dependent eigenvectors and eigenvalues of $\boldsymbol{R}(s)$. Then the result for uniform $\boldsymbol{c}_o$ and $\boldsymbol{c}_o^*$ is

$$\hat{c}_j^{\text{out}} = \sum_{j=1}^{N} \boldsymbol{x}^j \left[\boldsymbol{x}^j \cdot \boldsymbol{Z}^{-2}\left\{\boldsymbol{c}^f \frac{\hat{f}_o(s - w_j(s))}{s} + \left[\left(\boldsymbol{R}(s)(\text{diag}\,\boldsymbol{h})^{-1} + \boldsymbol{I}\right)\boldsymbol{c}_o^* + \boldsymbol{c}_o\right]\left(\frac{1 - \hat{f}_o(s - w_j(s))}{s - w_j(s)}\right)\right\}\right] \quad (12)$$

It is interesting to note that the matrix $\boldsymbol{R}(s)$ in question has many properties of a rate constant matrix. In particular if the chemistry is detailed balanced: it is symmetrizable at each s; its eigenvalues are real and nonpositive for all $s \ge 0$, and it does not have a zero eigenvalue unless $s = 0$; i.e., it does not have an equilibrium before infinite time. In addition, since the matrix in question is a function of s (the $s \longrightarrow 0$ limit of $s\hat{c}(s, \tau)$ for a fixed-bed reactor and, in particular, the $s \longrightarrow 0$ limit of $\boldsymbol{R}(s)$ is given in Eq. 7) limit, the rate constants (derived from the eigenvalues and eigenvectors) measured at steady state (i.e., at $s = 0$) are not applicable directly to dynamics. In principle, one would have to construct the dynamic matrix from the steady-state rate constants and the transform variable s, and then spectrally decompose the resulting matrix as a function of s for Laplace-transformed dynamic predictions. Accomplishment of this task, however, would require independent knowledge of $\boldsymbol{h}^*$, which, unfortunately, is not usually available.

It is worth noting that one can easily modify Eq. 12 to allow

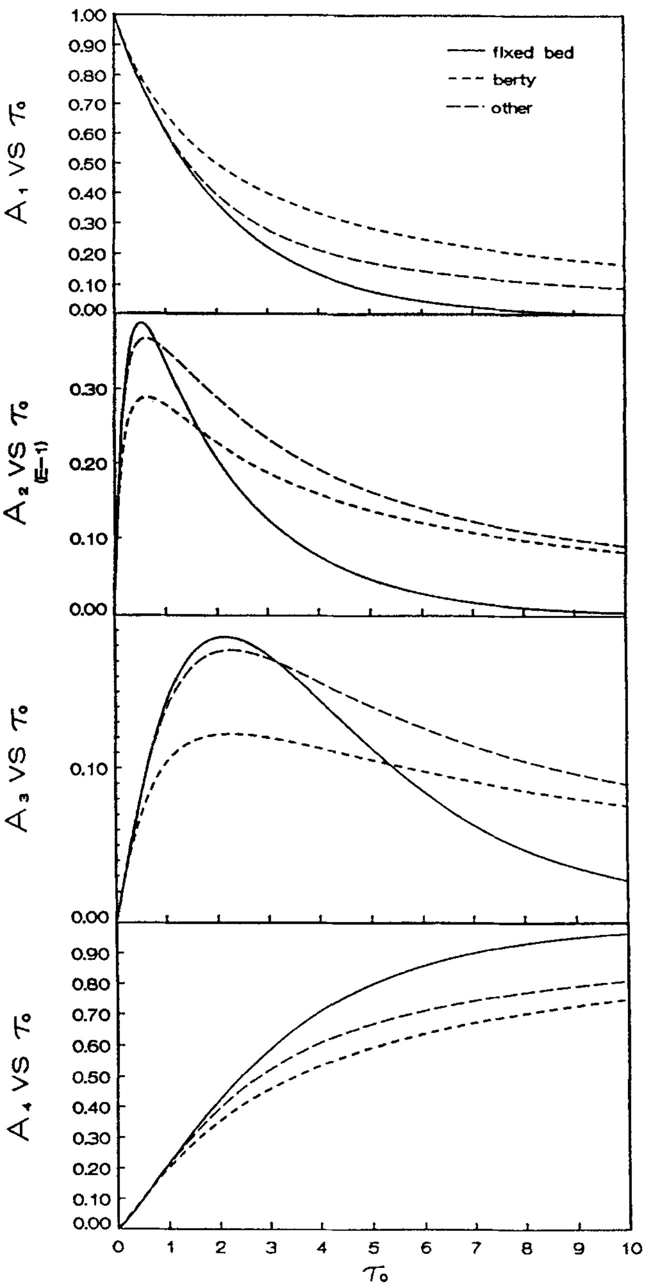

Figure 3. A comparison of the effluent concentrations of the reacting species as a function of τ_0 for reactors described in text.

The surface reaction mechanism is $A_1 \rightleftharpoons A_2 \rightleftharpoons A_3 \rightleftharpoons A_4$, with all parameter values given in the text.

A^* to be defective, as might be the case, say, in some biological application where the detailed balanced hypothesis would be inappropriate.

Despite this rather more involved dynamic treatment, the procedure outlined above represents an appreciably simpler mathematical treatment of the unsteady reaction-mass-transfer-flow problem than the solution of the system's detailed transport and reaction equations. Using a fixed bed, or, if it is more convenient, a Berty reactor, one can extract the $\{\omega_k(s)\}$, the $\{x^k(s)\}$ and the appropriate coefficients, and use the above discussion to scale to the design reactor. The problem considered here illustrates how linear systems may allow a separation of a reactor's reaction progress from all flow characteristics that do not enter into its appropriate residence time distribution analog, when such an analog exists. Applications of these results can be relevant not only in chemical reactors but also in chromatography and in biology (Hatton and Lightfoot, 1984).

Conclusions

The product distribution of heterogeneous reactors is quite complex. Luckily tracers experiments can sometimes be reliable tools and provide a framework for scale-up. We have demonstrated that certain types of two-phase, first-order reactors behave and scale as if they were single-phase, first-order reactors. However, the conditions under which this is valid are delicate indeed, being sensitive to, among other things, the choice of tracer. Tracer studies such as Figure 1 can provide significant help in identifying potential problem areas.

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Notation

a = coefficient in Eq. 1
A^* = surface reaction rate constant matrix
c, c^* = inner, outer phase concentration
c^f = feed concentration
c_o, c_o^* = inner, outer initial ($t = 0$) concentration
$C = (c, c^*)'$
e^i = ith natural basis vector
$f_o(\tau)$ = density function associated with nonadsorbing tracer
h, h^* = vectors of adsorption and desorption coefficients
i, j = species indices or state index
k_{ij}^* = rate constant for reaction $j \rightarrow i$ or probability of state transition $j \rightarrow i$
L = reactor length
M, N = numbers of outer and inner phase species, respectively
n = an integer
$p_{j;i}$ = conditional probability of returning to inner phase in state j given that molecule entered outer phase in state i^*
$\mathbb{R}$ = real numbers
$R(s)$ = matrix defined before Eq. 12 for $s \geq 0$ and by the square bracket in Eq. 6 for $s = 0$
s = Laplace transform variable
t = real time
$V = \mathbb{R}^N$
x^k = kth eigenvector of $R(s)$
$y^k(\tau_o)$ = kth eigenvector of matrix referred to below Eq. 11
z = axial position variable
Z = matrix defined just before Eq. 12

Greek letters

α = ratio of solid to void volume
δ = Dirac delta distribution
$\in$ = is a member of
ζ = stretching factor
$\theta_k(\tau_o)$ = eigenvalue belonging to $y^k(\tau_o)$
λ = eigenvalue of first-order chemical mechanism
$\omega_k(s)$ = eigenvalue belonging to $x^k(s)$
τ = inner phase age variable
τ_o, τ_p = average value of τ for reactor and its product with apparent catalyst density

Superscripts and subscripts

$\hat{}$ = Laplace transform
i, j = species index
out = refers to effluent

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