

A general formula for reactant conversion over a single catalyst particle in TAP pulse experiments

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Abstract

We obtain a general formula for reactant conversion in diffusion-reaction TAP systems over single non-porous catalyst particles as a product of two terms: $\alpha = P_H \times \mathcal{K}$.

The first term, P_H , is a purely geometric factor dependent only on the shape of the reactor and the shape and position of the catalyst particle, interpreted as the probability that an individual molecule of reactant will hit the catalyst before leaving the reactor. The second term, $\mathcal{K} = k\tau_H/(1 + k\tau_H)$, is a geometrical/chemical term involving the kinetic constant k and a transport characteristic (residence time in the catalyst zone, τ_H). Both P_H and τ_H can be effectively calculated for any given reactor-particle configuration. Our formula greatly extends the validity of a formula given in [Shekhtman et al., 1999] for thin-zone TAP-systems. It is derived by a probabilistic analysis of the residence time of individual molecular trajectories in chemically active regions. Our results are based on the theory previously developed in our paper [Feres et al., 2009].

1 Introduction

Information from single particle studies is intended to provide guidance in developing practical catalytic materials. Recently, results have been presented from a series of catalytic experiments using a single micron-sized catalyst particle surrounded by non-active quartz particles (so-called “needle in a haystack catalysis” [Zheng et al., 2008]). For example, heterogeneous CO oxidation over platinum catalyst experiments have been conducted at vacuum conditions and at atmospheric pressures using a TAP (Temporal Analysis of Products) reactor system, as described in [Gleaves et al., 1988, Gleaves et al., 1997, Pérez et al., 2007, Yablonsky et al., 2003]. The catalyst particle occupies less than 1% of the cross-sectional area of the microreactor so that the reaction zone may be regarded as a point source. This eliminates non-uniformity in reactant concentration and catalyst composition even in the domain of high conversion. The results are significant because they allow direct comparison between transient response experiments performed at vacuum conditions and steady flow experiments performed at atmospheric pressures, thus bridging the “pressure gap.” Also, use of a single particle opens the door to a variety of new non-steady-state experiments that can supply intrinsic kinetic information directly related to catalyst composition and structure. For example, the particle could be a well-defined single crystal, or an inert particle with metal deposited on its surface. Since all experiments use the same basic unit, namely, the catalyst particle, as well as the same reactor configuration and conditions, results from different experiments can be directly compared.

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Because TAP transient response experiments provide intrinsic kinetic data (e.g., number of active sites, site activation energy, etc.) and transport data, experiments performed on single crystals can be correlated with experiments performed on multi-crystalline materials. These experiments provide a new approach to bridging the materials gap.

In a single-pulse TAP-experiment, catalyst composition is changed insignificantly. Similar to our previous paper [Feres et al., 2009], we assume that the reaction is of first order, i.e., $R = kC_A$ where R is reaction rate, k is an apparent kinetic constant, and C_A is the reactant concentration for the apparent reaction of type $A \rightarrow B$. In this paper, by a ‘particle’ it is understood a piece of non-permeable catalyst with a specified shape and location in the reactor.

A catalyst particle can be small or big, spherical or cylindrical, foil shaped, etc. The only requirements we make are: uniformity of chemical composition and uniformity with regard to a locally defined notion of residence time on the reactive catalyst particle. The meaning of the latter uniformity condition will be explained shortly. The theory we are developing actually applies to systems with one or more particles, or to configurations containing regions permeable to gas flow composed of a large number of very small particles such as in thin-zone systems, as explained in [Feres et al., 2009]. For the sake of concreteness and given their special interest, however, we focus attention here on single particle systems, although a simple system in dimension one involving permeable catalyst units (thin zones) will be discussed later to illustrate a point in the theory.

Conversion is defined as the ratio

$$\alpha = \frac{N_0 - N}{N_0} \quad (1)$$

where N_0 is the pulse intensity, i.e., the number of molecules per pulse, and N is the number of reactant molecules leaving the reactor in the outflow mixture. A general method for calculating α , based on the solution of a time-independent boundary value problem, was obtained in [Feres et al., 2009], but the more detailed results in that paper applied only to systems with very fast reaction (infinite reaction constant k). In the present paper we go much further by showing that, for finite k , the general solution to the conversion problem admits a very simple description as a product

$$\alpha = P_H \times \mathcal{K}, \quad (2)$$

where P_H is a purely geometric term, referred to as the *hitting probability* (see further explanation below), which depends only on the shape of the reactor and the shape and position of the catalyst particle. \mathcal{K} , a geometrical/chemical term, i.e., dependent both on the geometric configuration of the system and the chemical activity of the catalyst particle. It takes the form

$$\mathcal{K} = \frac{\tau_H k}{1 + \tau_H k}, \quad (3)$$

where k is the kinetic constant. As will be explained in more detail in Section 4, the *conditional residence time* τ_H is a certain residence time in the vicinity of the catalyst particle that, similar to P_H , only depends on geometric information. P_H is interpreted as the probability that individual gas molecules will hit the catalyst before leaving the reactor. Both P_H and τ_H can be obtained for any given reactor/catalyst configuration by solving a boundary value problem for Laplace’s equation, as described and illustrated in [Feres et al., 2009]. They can also be obtained by direct stochastic simulation, which is the method we use in the present paper. The factor P_H in the above formula was analyzed in detail in our previous paper. Thus the most important result of the present one is that conversion in the finite k case, under very general geometric configurations of reactor/catalyst, takes the surprisingly simple form just explained. Properly interpreted, the term \mathcal{K} is very similar to the conversion formula for such configurations as thin-zone systems, which are essentially one-dimensional and can be studied very explicitly by analytic methods. So our present result opens up the way to analyze and interpret much more general configurations in terms that are already familiar from the study of thin-zone systems.

A formula for conversion in thin-zone TAP reactors, $\alpha = \tau k / (1 + \tau k)$, was first obtained in [Shekhtman et al., 1999] by very different means. It can also be derived as a particular case of 2 once the residence time τ in the thin-zone is reinterpreted in terms of our τ_H . For thin-zone reactors, it was found in [Shekhtman et al., 1999], and confirmed in [Feres et al., 2009] using our methods, that $\tau_H = \delta(L - x) / \mathcal{D}$, where $\delta = x_2 - x_1$ is the thickness of the zone, x_1, x_2 are the axial coordinates of the zone's beginning and end, $x = x_2$, L is the reactor's length, and \mathcal{D} is the gas diffusivity. Moreover, in the case of thin-zone reactors, gas molecules must necessarily reach the catalyst so $P_H = 1$ for those systems.

In our single particle case, numerical calculations indicate that for a cylindrical reactor with a small circular non-porous catalyst placed at axial coordinate x

$$\tau_H \propto \delta(L - x + a) / \mathcal{D} \quad (4)$$

where a depends on the radius of the catalyst foil (a parameter which is obviously not present in the thin-zone reactor), and a is close to zero if the catalyst radius is small. The parameter δ in 4 was introduced in [Feres et al., 2009] and is reviewed in Section 3. We think of it as the thickness of a region near the surface of the catalyst where gas molecules are susceptible of colliding with the catalyst surface and reacting. As noted in that paper, k and δ always appear together as a product, $k\delta$, in any expression of reactant conversion. In fact, Equation 11 in Section 4 shows that τ_H always contains the factor δ / \mathcal{D} for any reactor/catalyst configuration. Separating δ and k requires a more fully specified probabilistic model of reaction than the one which is adopted here and should be a topic of future theoretical and experimental study. Thus, as in [Feres et al., 2009], we regard $k\delta$ as an apparent reaction constant and do not attempt to specify δ separately.

In conclusion, given the similarities shown in this paper between the expression for reactant conversion in the general single particle case and in thin-zone systems, the latter case can serve as a useful guide for the behavior of the former.

The paper is organized as follows. Section 2 describes the reaction-diffusion system under study, which is a model TAP-system; Section 3 recalls the reaction model from [Feres et al., 2009] used in our analysis of conversion; Section 4 provides further information about the residence time term τ_H ; Section 5 illustrates some of the results by stochastic simulation of the diffusion-reaction system; Section 6 gives the mathematical derivation of the conversion formula; Section 7 illustrates the main results for simple one dimensional systems (thin-zone reactors), mainly for the purpose of clarifying a condition of *residence time-uniformity* needed in the derivation of the conversion formula. Finally, some conclusions are given in Section 8. The following rough guide to mathematical symbols may be useful: except for those that appeared in this introduction, most other symbols are specific to the section of the paper where they are read, so their definition can typically be found no more than a few paragraphs away.

2 The diffusion-reaction system

The typical first order reaction model used in TAP systems ([Feres et al., 2009, Gleaves et al., 1988, Gleaves et al., 1997, Shekhtman et al., 1999, Yablonsky et al., 2003]) is adopted here. A first order reaction of type $A \rightarrow B$, where A and B are gas species, is assumed to occur on the surface of a catalyst particle or foil placed inside a reactor as depicted in Figure 1. The reactor is packed with an inert material such as silica particles, forming a medium that is permeable to gas transport.

It is assumed that diffusion in the inert medium inside the reactor is Fickian and the gas is in the Knudsen regime (i.e., mean free paths are comparable to the interstitial spaces in the packed reactor). In this case molecular trajectories can be modeled as sample paths of a Wiener process (mathematical Brownian motion). Denoting by \mathcal{D} the diffusion constant of gas A in the inert

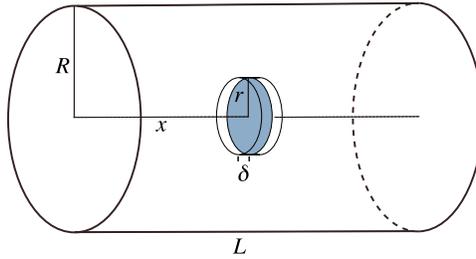


Figure 1: A cylindrical reactor of radius R and length L contains a circular catalytic metal foil of radius r at position x along the reactor axis. It is filled with an inert material that is permeable to gas transport. The back (or left) wall is closed except for a small passage at the center where a pulse of gas can be injected into the reactor; the front (or right) side is open to gas moving out of the reactor. The (microscopic) thickness parameter δ will be explained later. The main result (Equation 2) holds for general shapes and sizes of catalyst particle, but the numerical experiments discussed later are for a foil as depicted here.

medium, then individual molecular trajectories are described by a random function of time $X_t = \sigma B_t$ where $\mathcal{D} = \sigma^2/2$ is the diffusion constant and B_t is standard Wiener process (for which dB_t has variance dt). Figure 2 depicts a typical molecular trajectory.

Given an initial pulse of gas of species A , we wish to study the reactant conversion of the reaction, defined as the ratio of the number of molecules of type B over the total number of molecules in the reactor outflow. In particular, we wish to understand how the conversion depends on the reaction constant.

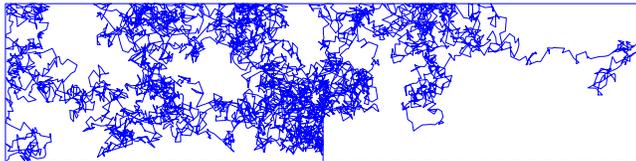


Figure 2: A typical molecular trajectory inside the reactor. The 3-dimensional reactor is here represented in cylindrical coordinates, only the radial, r , and axial x , but not the polar angle, being shown. The path is the projection of a 3-dimensional trajectory to the rx -plane. The point of injection is the center of the back wall, which corresponds to the lower-left corner of the rectangle. In this figure, and in all numerical experiments described later, the geometric parameters are: $L/R = 4$, $r/R = 0.3$, and $x/R = 2$.

3 The probabilistic reaction model

A central role will be played in our discussion by what is known in the stochastic processes literature as *local times* (see, for example, [Borodin et al., 1996, Itô et al., 1996]), although we deal with this concept here on a very informal level. Perhaps a more descriptive name for it is *residence (or occupation) time density*. Skipping over technical details, this concept can be defined as follows. Let p_0 and p be two point locations in the reactor and define the random number $\mathcal{O}_{p_0}(p, \delta)$ as the total amount of time that a random molecular trajectory, starting at p_0 at time $t = 0$, spends in a small spherical region of radius δ centered at p . Time is counted until the molecule leaves the reactor

in the gas outflow. If now $V(p, \delta)$ denotes the volume of that spherical region, then the *residence time density* at p is the limit of the quotient $\mathcal{O}_{p_0}(p, \delta)/V(p, \delta)$ for small values of δ . Thus, given an arbitrary region \mathcal{R} inside the reactor, the residence time in \mathcal{R} of a random molecular trajectory starting at p_0 is obtained by integrating the residence time density in the variable p over \mathcal{R} . The derivation of formula 3 requires an assumption which we refer to as *residence time uniformity*. This means that the residence time density at p is independent of the location p on the catalyst surface.

The symbol τ will be used to designate the residence time in a thin region of fixed thickness δ surrounding the catalyst surface.

We adopt here a simple probabilistic description of reaction used in [Feres et al., 2009]. It is based on the following idea, which essentially amounts to an operational definition of the reaction constant k : the probability that a molecule of type A converts into B is given by

$$p = 1 - e^{-k\tau}, \quad (5)$$

where τ is the residence time in some “chemically active” region in which the molecule is susceptible of reacting. It is then postulated that this active region consists of a small neighborhood of the catalyst particle having thickness δ . This active neighborhood is what is depicted in Figure 1 around the circular foil.

As already noted in the introduction, the parameter δ is left unspecified, whereas δk is viewed as the apparent kinetic constant for the first order reaction. There is no inconsistency in this since k and δ always appear together as a product. (Mathematically, this is due to the form of the second boundary condition for the function ψ below.) The length $\epsilon = \mathcal{D}/(k\delta)$ is independent of arbitrary choices and specifies the thickness of what may be regarded as a chemical boundary layer over the catalyst surface. This is discussed in more detail in Section 5.

In [Feres et al., 2009] it is shown that conversion can be obtained by solving a boundary value problem for Laplace’s equation, given as follows. We define a function $\psi(\mathbf{x})$, called the *survival function*, which gives the probability that a molecule of species A placed at \mathbf{x} in the reactor will exit without undergoing reaction. Thus,

$$\psi(\mathbf{x}) = E^{\mathbf{x}}[e^{-k\tau}], \quad (6)$$

where E denotes conditional expectation, given the initial point \mathbf{x} and τ , as already mentioned, is a random variable representing time in the active neighborhood. This survival function is harmonic, i.e., it satisfies Laplace’s equation $\nabla^2\psi = 0$, and boundary conditions (see [Feres et al., 2009]):

$$\mathbf{n} \cdot \nabla\psi = 0 \quad \text{on reactor walls} \quad (7)$$

$$\mathbf{n} \cdot \nabla\psi - \frac{k\delta}{\mathcal{D}}\psi = 0 \quad \text{on catalyst surface} \quad (8)$$

$$\psi = 1 \quad \text{on reactor exit} \quad (9)$$

where $\mathbf{n} \cdot \nabla\psi$ is the normal derivative. If \mathbf{x}_0 denotes the point of injection of gas into the reactor, then conversion is given by $\alpha(k) = 1 - \psi(\mathbf{x}_0)$. In the particular case of $k = \infty$, or very fast reaction, the second boundary condition reduces to $\psi = 0$ and ψ is interpreted as the probability of a molecule exiting the reactor without hitting the catalyst. We denote the hitting probability by P_H , so that

$$P_H = \alpha(\infty). \quad (10)$$

I.e., P_H is the reaction probability in the limit of infinitely fast reaction. In [Feres et al., 2009] we have calculated P_H for several catalyst configurations in 2-dimensional model reactors containing one or two units of catalyst (particles) of various simple shapes, by numerically solving the boundary value problem. For the 3-dimensional example of this paper, P_H is alternatively obtained by stochastic simulation, although the same boundary value problem could also be used.

4 The conditional residence time τ_H

The mean residence time in the thin active region *conditional* on the molecular trajectory hitting the catalyst, i.e., the expected amount of time a molecule spends in the active region assuming that it actually goes into the region at all, will be denoted τ_H . In general, the determination of τ_H , which is a purely geometric concept, requires solving the boundary value problem for the survival function ψ . This can be done very easily and explicitly in dimension 1 (thin-zone reactor; see [Feres et al., 2009]) but not so easily in general. Nevertheless, it is possible to give the following qualitative expression for the example of Figure 1:

$$\tau_H = \frac{R\delta}{\mathcal{D}} F(L/R, r/R, x/R), \quad (11)$$

where F is a dimensionless quantity that depends on the specific geometric features of a given reactor/catalyst configuration. (Obviously, for different configurations, geometric parameters other than L, R, r, x may be used.) This formula is derived in Section 6.

We have investigated the dependence of the function F on r/R and x/R numerically. Most interestingly, our calculations show that τ_H is very nearly a linear function of x/R for a fixed r . This is shown in Figure 3. Therefore, for a fixed r , F takes the form given by Equation 4. When r/R is very small and $L = x$, one clearly expects F to be nearly zero, so the term a given in Equation 4 should be negligible and we obtain the following expression for τ_H valid for a small single particle:

$$\tau_H = A \frac{\delta(L-x)}{\mathcal{D}}. \quad (12)$$

A more detailed description of the function F , including further information about the unspecified function A of r/R above will be left to a future study. We simply note, in passing, that the dependence on r/R for a fixed x observed in our numerical experiments is very nearly quadratic for $r < 0.8R$, and increases fast to ∞ as r approaches R . The latter property is to be expected since the catalyst naturally begins to block the passage of the gas out of the reactor when r approaches R .

As will be seen in Section 6, our derivation of the expression for \mathcal{K} (see equation 3) in terms of τ_H is partially justified by a numerical computation, hence it is not mathematically fully rigorous. A rigorous derivation requires adapting for our needs the theory of local times for Gaussian processes in dimension greater than one, which we plan to do in the near future in a more mathematical paper. (As a reference to this general topic, we recommend [Marcus et al., 2006].)

5 Determination of $\alpha(k)$ by stochastic simulation

Conversion can in principle be calculated in two different ways: by solving the boundary value problem for ψ or by direct stochastic simulation. In this section, we illustrate the use of the latter method.

Figure 4 was obtained by simulating the motion of 1000 molecules and by calculating for each the residence time, τ , in the active region, i.e., the total time the molecule spends in the neighborhood of thickness δ before leaving the reactor. If τ_1, \dots, τ_N are independent sample values of the random variable τ , then by the law of large numbers $\alpha(k) = 1 - E^{x_0}[e^{-k\tau}]$ is given by

$$\alpha(k) = 1 - \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{j=1}^N e^{-k\tau_j}. \quad (13)$$

In Figure 4 we have approximated $\alpha(k)$ using $N = 1000$. The 95% confidence interval around the empirical $\alpha(k)$ is also shown.

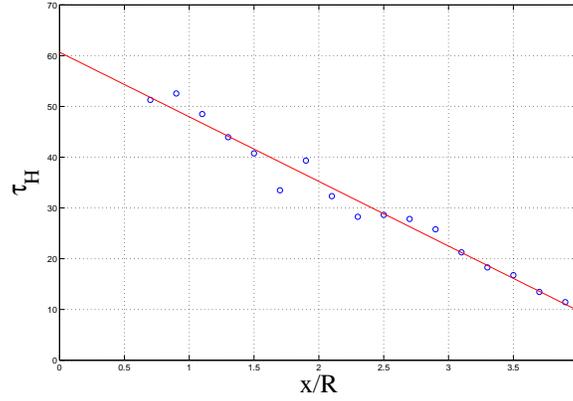


Figure 3: Dependence of τ_H on the axial position of the foil catalyst. The geometric parameters are: $L/R = 4$, $r/R = 0.3$, and $\delta/R = 0.05$. Linear interpolation gives $\tau_H \propto (L - x)/R + 0.69$.

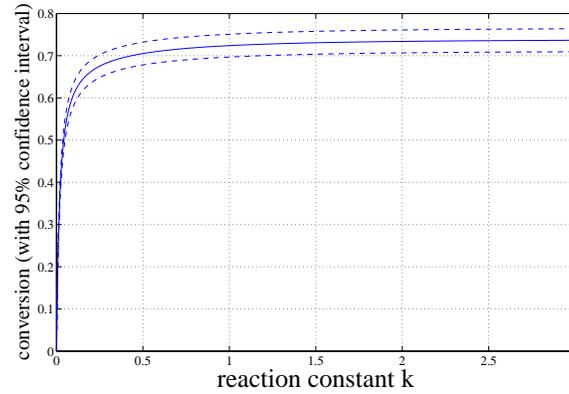


Figure 4: Conversion as a function of the reaction constant for $\delta = 0.05$. Simulation parameters: $L/R = 4$, $r/R = 0.3$, $x/R = 2$, $\delta/R = 0.05$, $D = \sigma^2/2 = 0.5$ ($\sigma = 1$), time step $dt = 0.001$. We have used $N = 1000$ in equation 13. The above curve is in very good numerical agreement with $\alpha(k) = P_H \tau_H k / (1 + \tau_H k)$, for $P_H = 0.74$ and $\tau_H = 44.0$, where P_H and τ_H were found by interpolation.

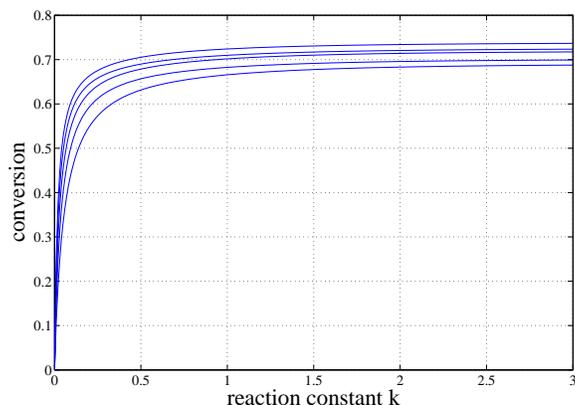


Figure 5: Conversion for several values of δ . From top to bottom: $\delta = 0.05, 0.04, 0.03, 0.02, 0.01$.

As pointed out earlier, our notion of k depends on a choice of δ , although α can also be viewed as a function of $k\delta/D$, which does not depend on arbitrary choices. Figure 5 shows how $\alpha(k)$ changes by changing δ . Figure 6 shows conversion for 4 different combinations of k, δ, D for the same $k\delta/D$.

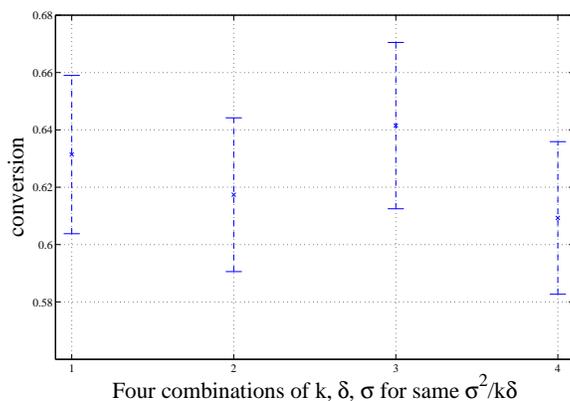


Figure 6: Conversion for various k, δ, D and same $k\delta/D$. The abscissa points 1, 2, 3, 4 stand for the following combinations of (k, δ, D) : $(0.5, 0.01, 0.5)$, $(0.4, 0.05, 2)$, $(2.0, 0.01, 2)$, $(0.1, 0.05, 0.5)$. The 95% confidence interval is indicated.

6 Derivation of the reactant conversion formula

The purpose of this section is to present a mathematical justification for our main formula. We have already defined the random variable τ , which gives the total time spent by a molecular trajectory in the neighborhood of thickness δ around the catalyst surface. We call τ the molecular *residence time* in that active neighborhood.

Knowing the conversion $\alpha(k)$, one gets the moments of τ . From Equation 13 it immediately

follows that the n th moment, $\langle \tau^n \rangle$, is given, up to a sign, by the n th derivative of $\alpha(k)$ at $k = 0$:

$$\alpha^{(n)}(0) = \frac{d^n}{dk^n} \left(1 - \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{j=1}^N e^{-k\tau_j} \right)_{k=0} = (-1)^{n+1} \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{j=1}^N \tau_j^n = (-1)^{n+1} \langle \tau^n \rangle. \quad (14)$$

In particular, the first moment satisfies: $\langle \tau \rangle = \alpha'(0)$.

It will be necessary to also consider the conversion function and moments of residence time *conditional on the molecule hitting the catalyst*. These quantities are defined as follows. Of the N independent trials, suppose that N_0 is the number of random trajectories that miss the catalyst entirely, so that the corresponding τ_j are 0, and $N_1 = N - N_0$ is the number of trajectories that hit the target before leaving the reactor, so that their τ_j are positive. After rearranging the order of the τ_j for simplicity of notation so that the first N_1 trajectories hit the catalyst, we obtain from 13:

$$\alpha(k) = \lim_{N \rightarrow \infty} \frac{N_1}{N} \left(1 - \frac{1}{N_1} \sum_{j=1}^{N_1} e^{-k\tau_j} \right) = P_H \alpha(k|\text{Hit}), \quad (15)$$

where P_H is the hitting probability and $\alpha(k|\text{Hit})$ is defined from Equation 15 and called the *conversion function conditional on hitting the catalyst*. Since $\alpha(\infty|\text{Hit})$ is clearly 1, we have $P_H = \alpha(\infty)$. I.e., conversion for very fast reactions is equal to the hitting probability.

If $\langle \tau^n | \text{Hit} \rangle$ denotes the conditional expectation of τ given that the molecule hits the catalyst, which we call the *conditional n th moment of τ* , the similar to Equation 14 we have

$$\alpha^{(n)}(0|\text{Hit}) = (-1)^{n+1} \langle \tau^n | \text{Hit} \rangle. \quad (16)$$

The conversion function $\alpha(k)$ is naturally a function of $k\delta/D$ and the geometric parameters R, r, L, x . From the equation $\langle \tau \rangle = \alpha'(0)$ and a simple dimensional analysis argument we obtain Equation 11. The same formula, up to the multiplicative constant P_H , holds for the conditional first moment.

Our derivation of 2 depends crucially on the following assumption: *For small δ , the random variable τ , conditional on hitting the catalyst, is exponential*. The precise mathematical conditions for the validity of this assumption are not fully clear at this point, and a more detailed discussion (which requires the theory of *local times* of diffusion processes, see [Marcus et al., 2006]) is planned for a future paper. Our justification for this here is both numerical and heuristic. First, the assumption is clearly supported by the stochastic simulation shown below (in this section). For the heuristic justification, we first recall that a continuous random variable S is exponential if it has the *memoryless property*, which states that for all $0 < s < t$, the conditional probability $P(S > t | S > s)$ equals $P(S > t - s)$. Supposing that the catalyst particle, referred to here by \mathcal{C} , is relatively small compared to the distance between itself and the reactor exit, (while δ is much smaller than the linear dimensions of \mathcal{C}), then the residence time in a thin δ -neighborhood of \mathcal{C} , given that it hits \mathcal{C} at all, is nearly independent of where on the surface of \mathcal{C} the molecule first hits. This is our assumption of uniformity of residence times over the catalyst referred to earlier. (The validity of this assumption will be explored in the next section in the setting of thin-zone reactors.) Thus, if t_1 and t_2 are two instants when a random molecular trajectory hits the catalyst, and S_1, S_2 are the respective remaining times spent in the δ -neighborhood (from t_1 or t_2 till the random moment the molecule exits the reactor), then S_1 and S_2 should have the same statistical properties. I.e., this residence time in the δ -neighborhood after a collision has the memoryless property characterizing an exponential distribution.

Figure 7 compares the distribution (histogram) of residence times for trajectories hitting the catalyst in a sample of 2000 trajectories ($\delta/R = 0.05$) with an exponential distribution whose

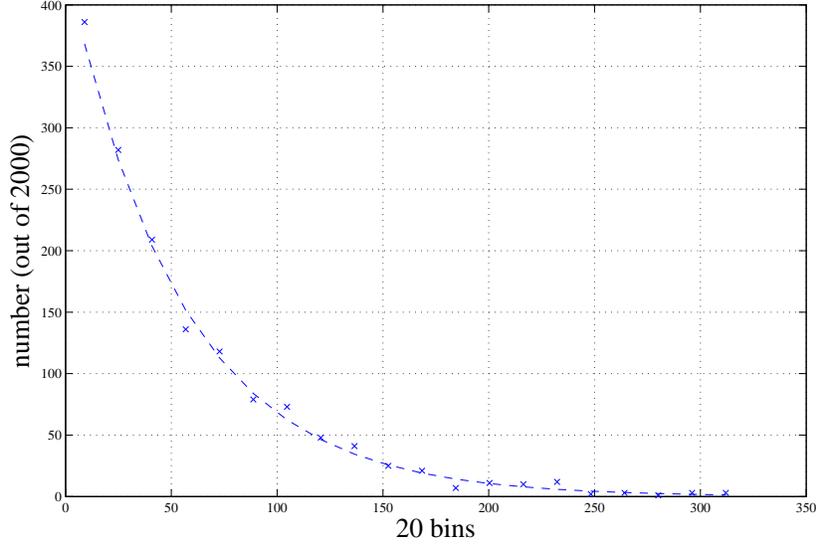


Figure 7: Histogram for the residence time in thin neighborhood (represented by crosses) compared to an exponential distribution whose parameter is the observed sample mean. Drawn from 2000 observations, approximately 70% of which are trajectories hitting the catalyst. So the total number of data points in the histogram is approximately 1400.

parameter is given by the sample mean. The graph strongly suggests that we are justified in assuming that the random variable is exponential.

Our main formula for conversion is now a consequence of the following well-known property of the moments of an exponential distribution:

$$\langle \tau^n | \text{Hit} \rangle = n! \langle \tau | \text{Hit} \rangle^n. \quad (17)$$

From this and the power series expansion of $\alpha(k)$ we obtain:

$$\begin{aligned} \alpha(k | \text{Hit}) &= \sum_{n=1}^{\infty} \frac{a^{(n)}(0 | \text{Hit})}{n!} k^n \\ &= \sum_{n=1}^{\infty} (-1)^{n+1} \frac{\langle \tau^n | \text{Hit} \rangle}{n!} k^n \\ &= \sum_{n=1}^{\infty} (-1)^{n+1} \langle \tau | \text{Hit} \rangle^n k^n \\ &= \frac{\langle \tau | \text{Hit} \rangle k}{1 + \langle \tau | \text{Hit} \rangle k}, \end{aligned}$$

where the last step gives the sum of an infinite geometric series. Using the notation $\tau_H = \langle \tau | \text{Hit} \rangle$, we obtain Equation 2. The equation is clearly in accordance with what was obtained by simulation in Figure 4, where P_H is shown in that specific case to be approximately 0.7.

7 Thin-zone systems and the time-uniformity condition

The derivation of our main formula was based on the assumption that the residence-time density is approximately constant over the catalyst zone. In this section we wish to investigate more closely the validity of this assumption. A system for which this can be tested very clearly consists of a number of thin catalyst layers that are permeable to gas flow. This is shown schematically in figure 8 for the special case of two layers. For such a system (with an arbitrary number of catalyst layers) the exact values for conversion, mean residence times, and hitting probability can be obtained analytically. (This type of system is also studied in [Constales et al., 2001-I, Constales et al., 2001-II] using a different approach.)



Figure 8: For this type of system, what was referred to before as a ‘catalyst particle’ corresponds to a thin active layer of catalyst, permeable to gas diffusion. The figure shows two layers of thickness δ_1, δ_2 placed at positions x_1, x_2 along the reactor axis, but the number of layers can be arbitrary. Gas is injected into the reactor at position x , which will be set equal to 0 in our calculations. The reactor end at l_2 is open to gas flow, whereas the end at l_1 may be closed or open. If it is closed, we set $l_1 = 0$ and $l_2 = l$, and if it is open, we set $l_1 = -l$ and $l_2 = l$.

We assume that the thickness of each layer is much smaller than any other length parameter associated to the reactor. We refer to the distance between the first and last layer as the *spread* of the catalyst zone. This is the distance $x_2 - x_1$ for the system of figure 8. The reactor can be regarded as being separated into three zones: the inert zone at the beginning, the catalyst zone in which we have lumped the thin active layers, and the inert end-zone. Let S denote the spread of the catalyst zone and l_{end} the length of the inert end-zone. Then it will be apparent from the below calculations that our main formula is valid when the ratio S/l_{end} is small.

We now show the exact values of P_H , τ_H and α for different configurations of the multi-layer system. The simple calculations are based on the theory developed in our paper [Feres et al., 2009]. As explained in that paper, the survival function $\psi(x)$ for these thin-layer systems satisfies the following conditions: (1) on any interval between l_1 and l_2 not containing an active zone, the second derivative $\psi''(x)$ is zero (so $\psi(x) = ax + b$, for some choice of a, b depending on the interval); (2) $\psi(x)$ is continuous across zones and the derivative $\psi'(x)$ has jump discontinuity at x_j given by $\psi'(x_j^+) - \psi'(x_j^-) = (k\delta_j/\mathcal{D})\psi(x_j)$; finally, $\psi(x)$ is 1 at the open ends of the reactor. If the end at l_1 is closed, then $\psi'(l_1) = 0$ there. These conditions yield a system of linear equations for the coefficients a, b of $\psi(x)$ at each interval between two x_j or between an x_j and one of the endpoints. Conversion is then given by $\alpha = 1 - \psi(0)$, assuming that the point of injection of gas is $x = 0$. Here is a short list of cases:

- If there is a single active layer and the reactor is closed at $l_1 = 0$, then the formula $\alpha = P_H \times k\tau_H / (1 + k\tau_H)$ holds for the following values of P_H and τ_H :

$$P_H = 1, \quad \tau_H = \frac{(l - z)\delta}{\mathcal{D}}. \quad (18)$$

- Suppose now that both ends of the reactor, at $\pm l$, are open and there is only one thin layer at

position $x_1 = z$. Gas is injected at the middle point ($x = 0$). Then

$$P_H = \frac{l}{l+z}, \quad \tau_H = \frac{(l^2 - z^2)\delta}{2l\mathcal{D}}. \quad (19)$$

- The reactor is assumed now to be closed at $l_1 = 0$ and there are two thin layers: one at x_1 with thickness $\delta_1 = \delta/2$, and another at x_2 with thickness $\delta_2 = \delta/2$. It is clear that, as in the first example, $P_H = 1$ since a molecule has to pass through an active layer before leaving the reactor. Let z denote the middle point between x_1 and x_2 . Then conversion is given by

$$\alpha = \frac{f(k)}{1+f(k)}, \quad \text{where } f(k) = \frac{k\delta}{\mathcal{D}}(l-z) + \left(\frac{k\delta}{\mathcal{D}}\right)^2 \frac{(l-x_2)(x_2-x_1)}{4}. \quad (20)$$

- Consider the same type of reactor as in the previous example, but now with three active layers at x_1, x_2, x_3 , each with thickness $\delta/3$. (For better comparison between examples, we have assumed in all cases a total thickness δ .) Let $z = (x_1 + x_2 + x_3)/3$. As in the previous example, $P_H = 1$ and $\alpha = f(k)/(1+f(k))$, for a function $f(k)$ given by:

$$\frac{k\delta}{\mathcal{D}}(l-z) + \left(\frac{k\delta}{\mathcal{D}}\right)^2 \frac{2(l-x_3)(x_3-x_1) + (x_2-x_1)(x_3-x_2)}{9} + \left(\frac{k\delta}{\mathcal{D}}\right)^3 \frac{(l-x_3)(x_2-x_1)(x_3-x_2)}{27}. \quad (21)$$

It is apparent that if the spread S of the catalyst zone is small compared to the length l_{end} of the inactive end-zone, then x_{j-1} and x_j are close to each other for all j and $f(k)$ is approximately $(k\delta/\mathcal{D})(l-z)$, where z is the center point of the distribution of the active layers. Thus we recover the expression $k\tau_H/(1+k\tau_H)$, where τ_H is the mean residence time in the active region consisting of the many layers, viewed together as one catalyst unit. (Since $P_H = 1$ in this case, the conditional residence time is the same as the residence time.) Similar formulas can be easily obtained for any number of layers: if m is the number of layers and the layers are located at x_1, \dots, x_m , then $\alpha = f(k)/(1+f(k))$, where $f(k)$ is a polynomial in $k\delta/\mathcal{D}$ of degree m whose coefficients are functions of x_1, \dots, x_m, l . The function $f(k)$ is computed as follows: Let $K = \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix}$ be the 2-by-2 matrix given by the product $K = K_m K_{m-1} \cdots K_2$, where

$$K_j = \begin{bmatrix} 1 + \frac{k\delta}{m\mathcal{D}}(x_j - x_{j-1}) & \frac{k\delta}{m\mathcal{D}} \\ x_j - x_{j-1} & 1 \end{bmatrix} \quad (22)$$

Then

$$f(k) = (l - x_m)a_{12} + a_{22} - 1 + \frac{k\delta}{m\mathcal{D}} ((l - x_m)a_{11} + a_{21}). \quad (23)$$

The above equations serve as a rough guide for how wide, or spread out, the catalytic region must be in general if our main formulas 2 and 3 for conversion should hold: if the catalyst units are lumped relatively close together compared to the distance between the catalyst lump and the reactor's end, it is expected that the formulas are valid.

When the active zone extends over a relatively large region of the reactor, then it is natural to ask how the conversion formula must be modified. Ideally, one would like to have a general formula in which the contributions of small elements of catalyst are integrated over the wider region, where an element is considered small if the residence time density is uniform over it. What such a formula should be like is something we are currently investigating.

8 Conclusions

We have shown that reactant conversion of a reaction-diffusion TAP system for an irreversible apparent first-order reaction and Fickian diffusion factorizes as a product $\alpha = P_H \times \mathcal{K}$ (equation 2) where P_H is a purely geometric factor interpreted as the probability that an individual molecule of reactant will hit the catalyst before leaving the reactor; and $\mathcal{K} = k\tau_H/(1 + k\tau_H)$, which is a geometrical/chemical term involving the kinetic constant k and a (conditional) residence time τ_H . Both P_H and τ_H can be effectively calculated based on the theory previously developed in our paper [Feres et al., 2009] for any given reactor-particle configuration. Our formula greatly extends the validity of a similar formula previously obtained for thin-zone TAP-systems. It is derived by a probabilistic analysis of the residence time of individual molecular trajectories in chemically active regions.

This formula can be considered as the main tool in a two-step procedure for TAP data analysis: (a) calculation of the (spatial) hitting probability, P_H , given the geometric characteristics of the reactor and catalyst particle (reactor length and radius, and particle size, shape and position) via the solution of the corresponding boundary value problem (see our paper [Feres et al., 2009]); (b) calculation of reactant conversion for a known kinetic constant (forward problem); or (c) determination of the apparent constant based on conversion data (backward problem). This equation can also be used for testing the transport model via change of catalyst particle position. We plan to present in the near future analysis of data relating to experiments of this kind.

9 List of symbols

α	reactant conversion
B_t	standard Wiener process (mathematical Brownian motion)
\mathcal{C}	(region occupied by) catalyst particle
\mathcal{D}	(Knudsen) diffusivity constant; $\mathcal{D} = \sigma^2/2$
δ	thickness of active zone near catalyst surface
ϵ	conversion is a function of the combined quantity $\epsilon = \mathcal{D}/k\delta$
$f(k)$	in thin zone systems, $\alpha = f(k)/(1 + f(k))$ for some function $f(k)$
$\langle \cdot \text{Hit} \rangle$	conditional expectation of some even (\cdot) given that molecule hits catalyst
k	kinetic constant
\mathcal{K}	geometric/chemical term in product formula for reactant conversion
K, K_j	matrices involved in the expression of α for multilayer thin-zone systems
L	Length of cylindrical reactor
N_0	pulse intensity (number of molecules per pulse)
N	number of reactant molecules leaving the reactor in outflow mixture
P_H	hitting probability (probability that random molecular motion will encounter catalyst)
p	probability of molecular conversion in $A \rightarrow B$ reaction. $p = 1 - e^{-k\tau}$
R	radius of cylindrical reactor
σ	standard deviation for random motion; $\sigma = 1$ for the Wiener process
τ	residence time in active zone
τ_H	residence time in active zone, conditional on event that molecular motion hits catalyst
x	axial coordinate along a cylindrical reactor
X_t	random molecular motion $= \sigma B_t$
ψ	survival function; conversion function for molecule starting at \mathbf{x} is $\alpha(\mathbf{x}) = 1 - \psi(\mathbf{x})$

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