

Probabilistic analysis of transport-reaction processes over catalytic particles: theory and experimental testing

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Abstract

We develop a probabilistic theory for conversion of $A \rightarrow B$ processes for a model Temporal Analysis of Products (TAP)-like experiments based on the general theory of Brownian motion with killing and the Feynman-Kac formula. Initial experimental testing for systems with a single catalyst particle is given, as well as numerical experiments for two-particle catalyst systems in simple geometric configurations.

1 Introduction

How to extract an intrinsic reaction rate for a chemical transformation over a catalyst particle from reaction-transport data? To answer this basic question, the TAP (Temporal Analysis of Products) technique was proposed by Gleaves in 1988, and it has been applied to many areas of chemical kinetics and engineering for non-steady state catalysis. ([Gle1, Gle2, Yab3]; see also the special issue of “Catalysis Today” [Per], released in 2007.)

Experiments described in this paper were carried out on a TAP-2 reactor system. The TAP-2 reactor system can be used to perform TAP vacuum pulse response experiments typically in the Knudsen diffusion regime (10^{-1} - 10^{-2} Pa) and atmospheric pressure steady-state, step-transient, and temperature programmed experiments. In a TAP Knudsen pulse response experiment, a narrow pulse of reactant gas is injected into a packed-bed reactor using a high speed pulse valve (figure 1). A typical microreactor is a stainless steel tube that contains an internal thermocouple and can be operated isothermally or temperature programmed. The microreactor is attached to a high-throughput vacuum chamber (10^{-8} - 10^{-9} torr) containing a UTI 100C QMS mass spectrometer. The reactor outlet and the mass spectrometer are separated by a 2-position slide valve assembly. When the slide valve is in the closed position, the reactor can be operated at atmospheric pressures (atmospheric flow experiments). In the open position the reactor operates at vacuum conditions (TAP pulse response experiments).

Unlike conventional transient response experiments, TAP vacuum experiments use no carrier gas, and each pulse contains a very small amount of reactant (approximately 10^{-9} moles/pulse). During a pulse, the gas density in the reactor drops rapidly and the molecular mean free path becomes greater than the distance between particles. As a result, reactant molecules and product

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molecules formed during chemical reaction move among the particles randomly and independently of one another. Gas transport through the reactor can be characterized as Knudsen diffusion, which has the property that the diffusivity of each gas in a mixture is independent of the composition of the mixture as a whole. Mathematically, a Knudsen pulse can be described using Fick's second law (diffusion equation); see a detailed analysis in [Yab4].

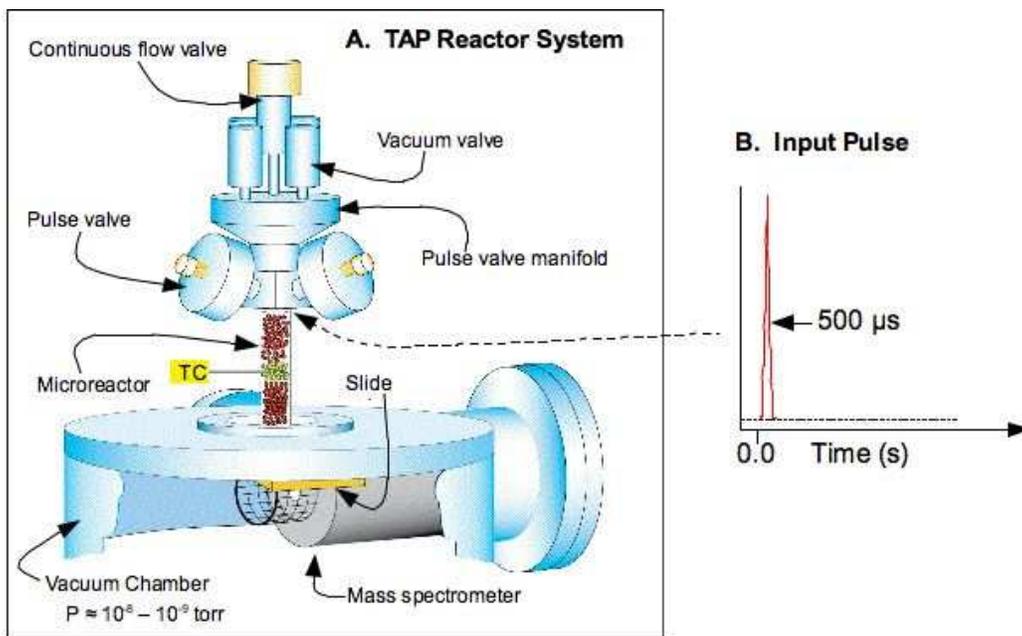


Figure 1: (A) Schematic of TAP-2 reactor apparatus, which consists of 3 main parts: the pulse valve manifold, reactor, and vacuum chamber containing the mass spectrometer. (B) Each inlet reactant pulse upon entering the reactor is a very narrow pulse, often represented by a delta function. The pulse broadens as it travels through the reactor, and in the case of an inert gas the pulse shape is the same as the standard diffusion curve.

The first configurations of the TAP-microreactor were the one-zone and three-zone reactor configurations. In the latter, the first and third zones are packed with inert material, and the middle zone is packed with the catalyst. These reactors were characterized by a significant concentration profile in the catalyst zone. Such non-uniformity makes extracting the rate of chemical transformation more challenging.

A third microreactor configuration is the thin-zone TAP-reactor (TZTR) proposed by Shekhtman and Yablonsky [Shek1]. The key idea of the TZTR is to make the thickness of the catalyst zone very small as compared to the length of the reactor. This keeps the change of gas concentration in the catalyst small compared to the maximum value of that concentration. The reactant conversion, denoted by α in the present paper, is determined by the simple relationship

$$\alpha = \frac{k\tau}{1 + k\tau}, \quad (1)$$

where k is the apparent reaction constant, τ is the diffusional residence time $\tau = \epsilon L_{\text{cat}} L_{\text{in2}} / D$, where ϵ is the porosity of the reactor bed (it is considered to be constant), L_{cat} is the width of the catalyst zone, L_{in2} is the width of the second zone packed with inert material, and D is the reactant diffusivity.

During a TAP pulse-response experiment the catalyst surface composition is approximately uniform in the TZTR. Thus it can be viewed as a “diffusional CSTR.” Detailed analysis of the uniformity and non-uniformity in the TZTR, and comparison with a differential plug-flow reactor (PFR) has been carried out in a series of papers [Shek1, Shek2, Shek3, Pha]. In the paper by Shekhtman and Yablonsky [Shek3] it was shown that diffusion operates as a mixing agent and decreases any non-uniformity created by the reaction. As a result the TZTR can be operated over a wide domain of conversions up to values as high as 80%. By comparison, a differential CSTR is typically operated at significantly lower conversions (below 20%) to maintain the required non-uniformity.

A fourth microreactor configuration, called a single-particle reactor, was recently described by Xiaolin Zheng et al. [XZhe]. The reaction zone is collapsed to the surface of a single micron-sized catalyst particle in a bed of inert particles. The particle occupies less than 0.3% of the cross-sectional area of the reactor, so the reactor zone can be considered a point source.

In a typical experiment, the reactor was packed with approximately 100000 quartz particles (210-250 microns in diameter) and a single catalyst particle (300 - 400 microns in diameter) usually positioned in the center of the bed. Results presented by Xiaolin Zheng et al. [XZhe] were obtained for particles of platinum (Pt) metal. Similar results were obtained using particles of alumina and quartz with a thin platinum deposit. The catalyst particle and the inert quartz particles are nonporous so that gas diffusion or mass transfer within particles does not occur.

It is clear intuitively that the single-particle TAP-reactor configuration has an important advantage even in comparison with the TZTR. Concentration and temperature gradients are negligible even at conversions higher than 80%. However, the theory of non-steady transport and reaction over a single particle surrounded by many non-active particles (catalytic “needle” in an inert “haystack”) is not developed. The goal of the present paper is to provide a theory. Our theory is probabilistic and is based on a “Brownian motion with killing” model of gas motion.

The way to compute conversion proposed in [Shek1] is to derive from the reaction-diffusion equations the zeroth moment of the flow rate, which equals 1 minus conversion. This was done before mostly for one dimensional systems. The main result of the present paper is that conversion can be obtained directly from the solution of a time independent boundary value problem that is technically much simpler than the corresponding reaction-diffusion equation for the system. Conversion for the thin zone reactor, equation 1, becomes an easy exercise for our equations. The new equations also apply in a straightforward way to very general spatial catalyst configurations, while it is not clear how to adapt the original approach used for the thin-zone reactor to more complicated systems. Of particular interest, the new approach can be used to analyze systems with a single catalyst particle of arbitrary form. After describing the boundary value problem for conversion, we give a preliminary account of a TAP system with a single catalyst particle both theoretically (numerically) and experimentally.

The paper is organized as follows.

- Sections 2, 3, 4, and 5 lay the groundwork for stating our main result, which consists of the boundary value problems (BVP) for obtaining conversion given in section 6. Section 2 gives the definition for conversion that we use in the paper and compares it with the equivalent definition used previously in other TAP papers in terms of the zero moment of reactant flow.
- Section 3 introduces the concept of a catalyst distribution function, η . This function specifies how a catalyst is distributed in the reactor and, together with the reaction constant k , determines the probability rate of reaction at each point inside the reactor.
- The main purpose of section 4 is to describe the various boundaries and other general concepts that are needed for setting up the BVP of section 6. The section also gives two examples of the catalyst distribution function η .

- Section 5 specifies the microscopic model for gas transport inside the reactor. It contains a very brief review of the definition of a Wiener process, also known as mathematical Brownian motion.
- Section 6 starts by stating the general form of the BVP. The solution is a function $\psi(\mathbf{x})$ called the *survival function* which gives the probability that a molecule of species A currently at position \mathbf{x} will leave the reactor without being converted into B . Thus the conversion α for a pulse of gas originating at position \mathbf{x}_0 is given by $\alpha = 1 - \psi(\mathbf{x}_0)$. Several special cases of the general problem are also shown. BVP 2 assumes that the active zone is the catalyst surface. BVP 3 assumes that the active zone is a thin porous surface. This case can be viewed as a special case of a pseudo-homogeneous catalytic medium composed of a large number of small particles. BVP 4 is a particularly useful limiting case that can be applied when the reaction $A \rightarrow B$ is very fast (high k limit).
- Section 7 uses the *thin zone* system to illustrate the various boundary value problems. The thin zone BVP can be solved very explicitly and easily by elementary calculations. It also serves as a test case for our method since it has been studied previously using a different method, by first solving the reaction-diffusion equation for the reactant gas concentration and then finding the zeroth moment of the reactant flow rate.
- Section 8 presents a numerical study, based on our BVP 4, of a simple 2-dimensional system containing a single catalyst particle. The purpose of the numerical experiment is to determine how conversion changes as a catalyst particle of fixed size and form is placed at different positions in the reactor. The main result of the section is given in the graph of figure 8, which shows conversion as a function of the x and y coordinates of the catalyst position for the system described in figure 6.
- Section 9 describes some experimental testing of the theory. It compares the results of section 8 with some preliminary TAP system data. Although precise comparisons cannot be made at this point (our numerical calculations are for model reactors that are very different than the actual TAP reactor: the model reactor is a 2-dimensional square with a square catalyst particle inside), the range and qualitative behavior of conversion as a function of the catalyst position are clearly similar. (See the graph of figure 9.) Similar numerical experiments simulating the precise geometry of a TAP reactor will be carried out in a future paper.
- In section 10 we describe calculations similar to those of section 8, but now for two-particle systems. An interesting new effect is observed here: there seems to be an optimal distance between the particles at which conversion is maximal. As the catalyst particles come closer than that distance, they start to behave as one single particle (i.e., conversion approaches the value obtained for just one of the particles), and when they move farther apart the diminishing yields observed in section 8 (and in the TAP experiments) take hold. A detailed study of multi-particle systems for more realistic TAP geometries, as well as experiments, will be done in a future paper.
- Section 11 summarizes the main conclusions. Finally, in a mathematical appendix we explain how the boundary value problems of section 6 are derived. The main probabilistic fact that we use is the so-called Feynman-Kac formula for a Brownian motion with killing, which we review and apply to the general TAP system.

2 Definition of conversion

In a TAP experiment, the typical measured quantities are the number of molecules that leave a reactor per second, F molec/sec, and the corresponding zeroth moment $\int_0^\infty F dt$, where t is time, or in dimensionless form

$$M_0 = \int_0^\infty \bar{F} dt$$

where $\bar{F} = F/N_p$ and N_p is the number of molecules pulsed into the reactor. If an irreversible reaction $A \rightarrow B$ is considered, gas collected at the open end of the reactor is a mixture of A and B . Conversion of reactant A is then represented as

$$\alpha = \frac{N_B}{N_A + N_B}, \quad (2)$$

where N_A and N_B are the numbers of moles of A and B , respectively. Conversion, α , and the zeroth moment, M_0 , of the dimensionless flow \bar{F} of A are related by

$$\alpha = 1 - M_0.$$

Figure 2 describes an idealized TAP experiment in which a pulse of gas of chemical species A is released into a chemical reactor and the outflow is collected at the right-hand open side, shown as a dashed line in the figure. The little black disc in the middle represents a particle of catalyst. (The catalyst particles are allowed to be arbitrary in number and form, and can have dimension 1, 2 or 3, but we use here a particle of simple shape for illustration.) It is surrounded by a chemically inert porous medium depicted by the smaller light colored dots.

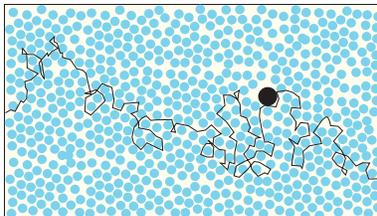


Figure 2: A reactor filled with an inert porous medium and the trajectory of a gas molecule from the point of injection to the open end of the reactor. The black circle indicates a catalyst unit. As A molecules come sufficiently near the catalyst unit, a reaction event $A \rightarrow B$ may occur. Gas collected at the open end of the reactor consists of a mixture of A and B . If initially all molecules are of species A , and if N_A , N_B are the total numbers of A and B molecules in the gas outflow, then conversion for the reaction is defined by $N_B/(N_A + N_B)$.

It is shown in this paper how conversion, α , can be derived from the distribution of catalyst. Towards this goal, we give a probabilistic interpretation of α that relates the definition given above to the random motion of individual A molecules inside the reactor. Before explaining this probabilistic definition of α , we need a function that represents the distribution of catalyst in the reactor bed. This is introduced in the next section.

3 The catalyst distribution function η

In this paper, the variety of configurations of the catalyst distribution is subsumed by essentially two main types. The first type corresponds to having only one or a small number of individually

identifiable non-porous particles with an arbitrary but specified form, such as spherical, foil, etc. Geometrically, a catalyst configuration of this kind is fully described by each particle's shape.

In the second type of configuration, we have a function over the space of the reactor giving the varying degrees of activity of the reactor medium. For example, parts or the whole of the reactor may be filled with a large number of small particles of catalyst which we do not want to regard individually but, instead, as constituting (by some appropriate averaging of positions) a continuous permeable catalytic medium. Therefore, instead of describing the form of active surfaces, this permeable medium is characterized by a function that gives the degree of activity at different places throughout the whole reactor. This function, which is defined more precisely below, will be denoted by η and will be called the *catalyst distribution function*. (The term *active zone function* will also be used occasionally.) If the reactor is filled uniformly with small catalyst particles, the catalyst distribution function is constant (equal to 1), whereas a variable function (between 0 and 1) represents variable concentration of catalyst.

There is another, more fundamental reason, for introducing the function η . Even when we regard catalyst particles individually, in order to model the process of adsorption (and subsequent reaction) of gas molecules probabilistically, we need to assume that each particle is surrounded by a thin active layer (the term *collar region* is used later) of a given thickness δ . In this region the degree of activity is specified by an $\eta(\mathbf{x})$ which is approximately 1 when \mathbf{x} is very close to the catalyst surface and becomes 0 for \mathbf{x} a small distance away from the surface. Therefore, the catalyst surface has a somewhat “diffuse” quality that is precisely characterized by a function η . In all cases, η contains information of a geometric nature, independently of any reaction constant.

These various types can be combined in different ways. Our general model of catalyst distribution, for the purpose of stating the boundary value problems for conversion later on, is formally expressed as follows. We separate the total space inside our model reactor into two regions, denoted by \mathcal{R} and \mathcal{S} . The former is the *permeable region*, which is accessible to gas molecules through diffusion. The latter is the region occupied by a non-permeable medium which, typically, corresponds to the internal space of a non-porous solid catalyst.

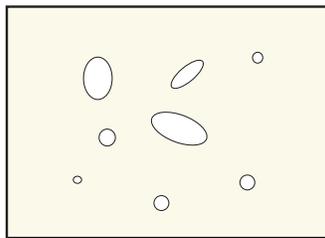


Figure 3: The region \mathcal{R} accessible to gas molecules is the part of the rectangle not including the oval shapes representing the catalyst particles. The latter region (union of the spaces occupied by individual catalyst particles) is denoted \mathcal{S} . The boundary surface of \mathcal{S} is denoted $\Gamma_{\mathcal{S}}$ (light solid lines in the figure) and the inner surface of the wall of the reactor, represented by the thick solid line, is denoted $\Gamma_{\mathcal{R}}$. The union of $\Gamma_{\mathcal{R}}$ and $\Gamma_{\mathcal{S}}$ will be called the *reflecting boundary* of \mathcal{R} . The dashed line represents the *exit boundary*, Γ_{exit} .

In \mathcal{R} , we imagine that catalyst activity is distributed essentially continuously and specified by $\eta(\mathbf{x})$, where \mathbf{x} is the coordinate vector in \mathcal{R} . Therefore, \mathcal{R} is the natural domain of definition of η . Also note that the surface boundary of \mathcal{R} will in general consist of three pieces:

1. The boundary surface, $\Gamma_{\mathcal{S}}$, of the impermeable medium \mathcal{S} ;
2. The walls of the reactor, $\Gamma_{\mathcal{R}}$; and

3. The exit surface, Γ_{exit} , through which molecules leave the reactor.

In other words, the total boundary Γ_{reactor} is the union

$$\Gamma_{\text{reactor}} = \Gamma_{\mathcal{R}} \cup \Gamma_{\mathcal{S}} \cup \Gamma_{\text{exit}}.$$

We now turn to the probabilistic definition of function $\eta(\mathbf{x})$. This is a dimensionless quantity with values between 0 and 1 that gives, together with the reaction constant k , the propensity for A molecules to react at any given place \mathbf{x} . In other words, if a molecule of type A remains near \mathbf{x} for a period of time dt , then $\eta(\mathbf{x})$ is defined by the property that a reaction will occur during that period of time with probability $k\eta(\mathbf{x})dt$. An equivalent, but still informal, definition of η is that, during the time that an A molecule remains near \mathbf{x} in the course of its random motion in the packed bed of the reactor, the probability that it does not react decreases exponentially in time with rate $k\eta(\mathbf{x})$ (while the molecule remains near \mathbf{x}). If $\eta(\mathbf{x}) > 0$, then a molecule of species A placed at \mathbf{x} is sufficiently near the catalyst to be affected by it and possibly react. In a region where η equals 1, the reaction proceeds with probability rate k . If, on the other hand, \mathbf{x} is far from where catalyst particles are located then $\eta(\mathbf{x}) = 0$ and the probability of reaction while the molecule remains near \mathbf{x} , for any amount of time spent at that location, is 0.

The following more precise, but essentially equivalent, formulation will serve as our definition of η . We first define the notion of molecular *residence time in active zones*. Let X_t denote the position of an individual molecule inside the reactor at time t , starting at $X_0 = \mathbf{x}_0$. This is a random function of t which does not have to be specified at this moment. (It will be modeled later by the so-called *Wiener process*, also known as *mathematical Brownian motion*.) Let T denote the (random) time at which a molecule leaves the reactor. Then η is defined as a function of \mathbf{x} that determines the total time a molecule spends in an active zone according to the expression

$$\tau = \int_0^T \eta(X_t) dt.$$

Hence τ can be thought of as a weighted residence time in the reactor, and η is defined as a weight function that assigns greater weight to places likely to be chemically active. To complete the definition of η , we assume that the probability of reaction during the time a molecule remains in the reactor is given by

$$p = 1 - e^{-k\tau}.$$

Thus $k\eta$ is a *probability rate of state transition*, a concept from the general theory of continuous time Markov chains. The examples of η given in the next section should help clarify the concept.

It is now clear how conversion, α , should be defined probabilistically, given η and the residence time in active zones, τ . The expected probability that an A molecule does not convert by the time it leaves the reactor is $\psi_0 = E^{\mathbf{x}_0} [e^{-k\tau}]$, where $E^{\mathbf{x}_0}$ denotes mathematical expectation, conditional on the molecule starting at \mathbf{x}_0 . This is the average of the probability of non-conversion over all the possible random trajectories the molecule may follow until exit. We now define conversion by $\alpha = 1 - \psi_0$. Note that ψ_0 agrees with the first moment M_0 defined earlier.

It is convenient to introduce more generally the function

$$\psi(\mathbf{x}) = E^{\mathbf{x}} [e^{-k\tau}], \tag{3}$$

where \mathbf{x} represents an arbitrary place in the packed bed of the reactor that gas molecules can occupy. We interpret $\psi(\mathbf{x})$ as the probability that an A molecule that is presently ($t = 0$) at \mathbf{x} will exit without conversion. We call ψ the *survival function* obtained from the catalyst distribution η . If at any given time there are N molecules of species A around \mathbf{x} , then we should expect that approximately (in the sense of the law of large numbers) $\psi(\mathbf{x})N$ of those molecules will not have

been converted after they have all left the reactor. Thus, expressed in terms of the survival function, conversion has the form

$$\alpha = 1 - \psi(\mathbf{x}_0). \quad (4)$$

The main theoretical point of the paper is that the survival function ψ , hence conversion α , can be computed by a standard type of boundary value problem, via the so-called *Feynman-Kac formula*. This will be explained shortly.

4 Examples of η

If the catalyst is a single spherical particle of radius r and center \mathbf{c} , and if a molecule of type A has to be a distance less than δ away from the surface of \mathcal{S} to be under the influence of the catalyst, then a natural choice of η is as follows (see figure 4):

$$\eta(\mathbf{x}) = \begin{cases} 1 & \text{if } |\mathbf{x} - \mathbf{c}| \leq r + \delta \\ 0 & \text{if } |\mathbf{x} - \mathbf{c}| > r + \delta. \end{cases}$$

In this example, \mathcal{S} is the region defined by $|\mathbf{x} - \mathbf{c}| < r$ (the white circular core in figure 4) and is not part of \mathcal{R} . Notice that the part of \mathcal{R} where $\eta(\mathbf{x}) = 1$ consists of a collar of width δ around the spherical particle, outside of which we have $\eta(\mathbf{x}) = 0$.

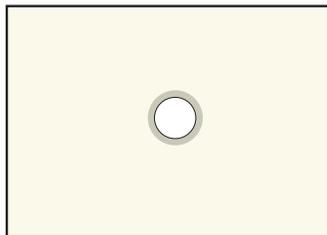


Figure 4: The active zone function is the indicator function of a collar region of thickness δ around the sample catalyst surface.

Figure 4 illustrates the concept of a collar of width δ , but is only schematic. One should expect δ in this case to be very small compared to the linear dimensions of \mathcal{R} , so the collar region around the catalyst particle shown in figure 4 should be much thinner than depicted. For the purpose of understanding the effect that the spacial distribution of catalyst has on conversion, it makes sense to think of δ as an unknown but constant “thickness” parameter that does not depend on the catalyst configuration.

In figure 5, the active region consists of a large number of small catalyst particles, each with a thin active collar zone around itself. They are surrounded by inert particles of comparable size. Here it is useful to regard \mathcal{R} as the whole interior of the reactor (so \mathcal{S} is empty) and to approximate η by a continuous function of the axial coordinate, as described in figure 5.

The approximation of $\eta(\mathbf{x})$ by a continuous function can be formally achieved as follows: Let $B(\mathbf{x}, a)$ denote a small spherical region around \mathbf{x} of radius a , where a is a scale parameter defining how coarse-grained a description of η we are willing to accept. Let V be the volume of the part of \mathcal{R} contained in $B(\mathbf{x}, a)$, and W the volume of the region in $B(\mathbf{x}, a)$ occupied by the collar regions. Then take $\eta(\mathbf{x}) = W/V$. Thus η is directly related to the concentration of catalyst particles in the packing of inert particles.

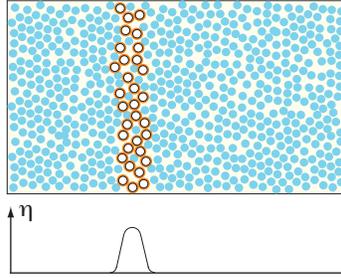


Figure 5: A thin layer of active particles sandwiched between inert particles. The active zone function η has the approximate form shown by the graph. In this case, we regard η as a function of the position along the axis of the reactor.

5 Brownian model for molecular motion

We need now to specify the model for molecular motion inside the packed bed of the reactor. The interior of the reactor is regarded as a porous medium in which gas of type A has diffusion constant D . (It will be apparent that, for the problem of finding conversion α of the irreversible reaction $A \rightarrow B$, only the diffusivity of A is relevant.) So the transport of gas A , away from active zones (i.e., ignoring reaction), is governed by the equation

$$\frac{\partial c}{\partial t} = D\nabla^2 c$$

where c is the concentration of gas of type A . The microscopic motion of gas molecules satisfying this diffusion equation can be approximated, for short mean free path, by

$$X_t = \sqrt{2D}B_t \tag{5}$$

where B_t represents the standard Wiener process (also referred to as mathematical Brownian motion).

For completeness, we recall the definition of B_t . It is a stochastic process in dimension n , where for us n may be 1, 2 or 3, having the following properties:

1. The random path $t \mapsto B_t$ is continuous;
2. The increments $B_{t+h} - B_t$, for positive h , are statistically independent of the position B_s for all past times $s \leq t$;
3. The displacement $\Delta B_t := B_{t+h} - B_t$ is normally distributed with mean 0 and variance h , independent of t . This means that if U is any region of n -dimensional space, the probability that ΔB_t lies in U is

$$P(\Delta B_t \text{ in } U) = \frac{1}{(2\pi h)^{n/2}} \int_U e^{-\frac{|x|^2}{2h}} dV(x)$$

where we use the notation $|x|^2 = x_1^2 + \dots + x_n^2$ and $dV(x) = dx_1 \dots dx_n$.

More concretely, we can think of X_t as proceeding as follows: if the molecule is at X_t at time t , then at time $t + dt$ it is at $X_{t+dt} = X_t + \sqrt{2D}dtZ$, where Z is a random variable in n -space having standard normal distribution.

Brownian motion in the reactor space \mathcal{R} is defined by essentially the same properties as in open space except that it is subject to reflection on the reactor walls and on the catalyst surface, and it is “killed” at the exit boundary (or open side) of the reactor.

6 Boundary value problems for conversion

We are finally in a position to state the main theoretical result. First, we summarize the main notation: let a catalyst distribution function $\eta(\mathbf{x})$ be defined on the accessible region \mathcal{R} of the reactor; suppose that gas transport is given by Fickian diffusion with diffusivity D (microscopically, this corresponds to the random motion described in section 5); let k be the reaction constant; let H denote the operation on functions defined by $H = -D\nabla^2 + k\eta$, where ∇^2 is the Laplacian; we write $H\psi = -D\nabla^2\psi + k\eta\psi$. Recall that conversion α can be calculated from the survival function $\psi(\mathbf{x})$ defined in section 3 by $\alpha = 1 - \psi(\mathbf{x}_0)$, where \mathbf{x}_0 is the position where a pulse of A -molecules is injected in the reactor.

The main result is that $\psi(\mathbf{x})$ is a solution for the boundary value problems (BVP) listed below. It will be useful for the applications we envisage to state different versions of the problem. The first version is the most general. The other versions are obtained by adding natural assumptions about the catalyst. Their essential difference has to do with where in the system the reaction is assumed to take place:

1. BVP 1: In this case, the reaction can occur anywhere on the permeable medium. The catalyst distribution is represented by a general distribution function η , which is included in the reaction term $k\eta$ of the reaction-diffusion operator H . The entire boundary surface (including Γ_S) is regarded simply as a reflecting boundary (i.e., no reaction directly on this surface);
2. BVP 2: the permeable medium \mathcal{R} is inactive and reaction only takes place on Γ_S . This is a limiting case of the first BVP, by regarding the active zone of the permeable medium \mathcal{R} as being very concentrated near Γ_S . Notice how a thickness parameter, δ , of an active boundary layer around Γ_S appears in the second boundary condition in the constant combination $\delta k/D$;
3. BVP 3: the permeable medium is the whole of the reactor space, but reaction may only occur within a very narrow region represented by a surface Γ . This case is a direct generalization of the *thin zone* TAP system studied in [Shek1];
4. BVP 4: here, similar to BVP 2, reactions only happen on the boundary surface of the impermeable region, but now we assume that the reaction constant k is infinite; i.e., we consider the limiting case of very fast reaction. In this case, conversion α is simply the probability that any given gas molecule will hit the catalytic surface before leaving the reactor.

In each of the below systems, the first equation is the time independent partial differential equation for the survival function ψ . The other equations are boundary conditions. In all cases, the last boundary condition, $\psi = 1$ on Γ_{exit} , expresses the fact that the survival probability $\psi(\mathbf{x})$ (i.e., the probability that an A molecule at \mathbf{x} will leave the reactor through Γ_{exit} without converting to B) is 1 if \mathbf{x} is right on that exit boundary. The symbol $\mathbf{n} \cdot \nabla\psi$ denotes the normal derivative at a point of a reflecting boundary with normal direction \mathbf{n} . Thus $\mathbf{n} \cdot \nabla\psi = 0$ is the standard Neumann (reflecting) boundary condition typically used to represent zero flux. (Notice, however, that ψ is not directly related to gas concentration, so it is not meaningful in this case to interpret zero normal derivative as zero gas flux through a boundary surface.)

Boundary value problem 1 (general form)

$$\begin{aligned} H\psi &= 0 \text{ on } \mathcal{R} \\ \mathbf{n} \cdot \nabla\psi &= 0 \text{ on } \Gamma_{\mathcal{R}} \cup \Gamma_S \\ \psi &= 1 \text{ on } \Gamma_{\text{exit}}. \end{aligned}$$

Here, the catalyst distribution is expressed in the “reaction term” $k\eta\psi$ that appears in the differential operator H . The other boundary conditions are either purely reflecting (second equation) or absorbing at the exit boundary (third equation).

Boundary value problem 2 (reaction on boundary layer over catalyst)

$$\begin{aligned}\nabla^2\psi &= 0 \text{ on } \mathcal{R} \\ \mathbf{n} \cdot \nabla\psi &= 0 \text{ on } \Gamma_{\mathcal{R}} \\ \mathbf{n} \cdot \nabla\psi - \frac{\delta k}{D}\psi &= 0 \text{ on } \Gamma_{\mathcal{S}} \\ \psi &= 1 \text{ on } \Gamma_{\text{exit}}.\end{aligned}$$

Physically, the active zone is, here, a very thin layer over the catalyst so that we can regard reactions as taking place on the boundary component $\Gamma_{\mathcal{S}}$. In this way, the reaction term (the constant k) is moved from the operator H , which becomes $-\nabla^2$ (reflecting pure diffusion in the permeable part \mathcal{R}), into one of the boundary conditions (third equation). This version of the boundary value problem 1 is more natural in a situation as represented by figure 4 in which the catalyst particle is relatively big and the active region is a thin layer of very small thickness δ . It is shown in appendix A how boundary value problem 2 is derived from boundary value problem 1.

Boundary value problem 3 (thin active permeable layer)

$$\begin{aligned}\nabla^2\psi &= 0 \text{ on } \mathcal{R} \\ \mathbf{n} \cdot \nabla\psi &= 0 \text{ on } \Gamma_{\mathcal{R}} \\ \mathbf{n} \cdot \nabla^+\psi - \mathbf{n} \cdot \nabla^-\psi - \frac{\delta k}{D}\psi &= 0 \text{ on } \Gamma \\ \psi &= 1 \text{ on } \Gamma_{\text{exit}}.\end{aligned}$$

This is a limiting case of the first BVP in which the region where η is not 0 reduces to a very thin surface Γ of thickness δ , with a large value for k . Notice that Γ is a permeable surface layer. The third equation (second boundary condition) should be compared with a mass-balance equation expressing surface reaction in terms of a “flux” discontinuity. We stress, however, that this interpretation is not directly valid since ψ does not represent concentration of gas, but survival probability. An example of this BVP is worked out in detail in section 7.

Boundary value problem 4 (large k approximation)

$$\begin{aligned}\nabla^2\psi &= 0 \text{ on } \mathcal{R} \\ \mathbf{n} \cdot \nabla\psi &= 0 \text{ on } \Gamma_{\mathcal{R}} \\ \psi &= 0 \text{ on } \Gamma_{\mathcal{S}} \\ \psi &= 1 \text{ on } \Gamma_{\text{exit}}.\end{aligned}$$

If the reaction constant k is very big, it is natural to simplify the problem by assuming that this constant is actually infinite so that a reaction takes place as soon as an A molecule comes in contact with $\Gamma_{\mathcal{S}}$. Therefore, the survival function $\psi(\mathbf{x})$ reduces to the probability that an A molecule presently at \mathbf{x} will leave the reactor without ever colliding with the catalyst. Notice that the function η , the reaction constant k , and the diffusion constant D do not appear in this system of equations. Information about the catalyst distribution is entirely contained in the description of the region \mathcal{S} . Thus the survival function is a harmonic function ($\nabla^2\psi = 0$) taking values 0 on $\Gamma_{\mathcal{S}}$

(survival probability is 0 right on the surface of catalyst), 1 on Γ_{exit} (survival probability 1 at the exit boundary) and reflecting boundary condition on $\Gamma_{\mathcal{R}}$.

These equations are illustrated next with a problem in one dimension that can be solved analytically. More complicated geometries in two dimensions will be analyzed numerically using the third version of the boundary value problem in a later section of this paper.

7 Thin zone

We now illustrate the boundary value problem for the survival function ψ with a one-dimensional example. The reader is referred to figure 5, describing a thin active zone inside the reactor. The catalyst function η of figure 5 will be approximated by a step function of the axial coordinate x . Let L be the length of the reactor. The accessible space is $\mathcal{R} = [0, L]$ and we suppose that the active zone is the interval $l_1 \leq x \leq l_2$. Then the function η can be written as follows:

$$\eta(x) = \begin{cases} 1 & \text{if } x \text{ in } [l_1, l_2] \\ 0 & \text{if } x \text{ in } [0, l_1) \text{ or } (l_2, L] \end{cases}$$

We assume that gas of species A is injected into the reactor at 0 and the outflow is collected at L . Below we find conversion α in different ways to illustrate the use of the different boundary value problems.

7.1 Finding α via BVP 1 (general form)

Conversion is given by $\alpha = 1 - \psi(0)$, where $\psi(x)$ is the solution to the first boundary value problem:

$$\begin{aligned} D\psi'' - k\eta\psi &= 0 \\ \psi'(0) &= 0 \\ \psi(L) &= 1. \end{aligned}$$

We impose on ψ and ψ' continuity at l_1 and l_2 . This problem is easily solved by elementary means. We write $\nu = \sqrt{k/D}$. Then the function $\psi(x)$ takes the form:

$$\psi(x) = \begin{cases} a & \text{if } x \text{ in } [0, l_1] \\ Ae^{\nu x} + Be^{-\nu x} & \text{if } x \text{ in } [l_1, l_2] \\ b + (x - l_2)(1 - b)/(L - l_2) & \text{if } x \text{ in } [l_2, L] \end{cases}$$

The constants a, b, A, B are given by:

$$\begin{aligned} a &= [\cosh(\nu(l_2 - l_1)) + \nu(L - l_2) \sinh(\nu(l_2 - l_1))]^{-1} \\ b &= a \cosh(\nu(l_2 - l_1)) \\ A &= \frac{a}{2} e^{-\nu l_1} \\ B &= \frac{a}{2} e^{\nu l_1}. \end{aligned}$$

Conversion α is then $1 - \psi(0) = 1 - a$, so

$$\alpha = 1 - a.$$

Under the assumption that $\nu(l_2 - l_1)$ is small (that is, the catalyst sample occupies a thin zone) the expression for α simplifies. Using that $\cosh \epsilon$ and $\sinh \epsilon$ are approximately 1 and ϵ , respectively, if ϵ is small, then α reduces to the following expression:

$$\alpha = \frac{k\tau}{1 + k\tau} \quad (6)$$

where $\tau = (L - l_2)(l_2 - l_1)/D$. It makes sense to interpret τ as a measure of the total time that molecules on average spend in the thin zone. This value of α is exactly the same as in equation 1, which was first obtained by solving for the reactant concentration and computing the zeroth moment of the reactant flow rate.

7.2 Finding α via BVP 3 (thin active permeable layer)

Equation 6 can be obtained more easily using boundary value problem 3. The equations are as follows (ψ is assumed continuous along the length of the reactor and $\psi'_{\pm}(l)$ denote the limits of the derivative from the left and right at l):

$$\begin{aligned} \psi'' &= 0 \\ \psi'(0) &= 0 \\ -\psi'_-(l) + \psi'_+(l) &= \frac{k\delta}{D}\psi(l) \\ \psi(L) &= 1 \end{aligned}$$

This system of equations is easily solved, and we get $\psi(0) = 1/(1 + k\tau)$, giving the same α as above. Notice the condition for an ideal thin zone: if δ is regarded as infinitesimally small, k should be big so that the constant $k\delta$ remains finite.

7.3 Finding α via BVP 4 (infinite k limit)

We now look at the limit for large k , under the simplifying assumption of thin zone limit. This means that ν is small even if we take k itself big (therefore, $l_2 - l_1$ must be very small). It is then clear that α approaches 1 and that the survival function $\psi(x)$ takes the following form (notice that we take $l_1 = l_2 = l$ in the expression below):

$$\psi(x) = \begin{cases} 1 & \text{if } x \leq l \\ (L - x)/(L - l) & \text{if } l < x \leq L. \end{cases} \quad (7)$$

This also follows from the boundary value problem 4 (large k limit). In this case, \mathcal{R} is the union of intervals $0 < x < l$ and $l < x < L$, and the boundary components are: $\Gamma_{\mathcal{R}} = \{0\}$, $\Gamma_{\mathcal{S}} = \{l\}$, and $\Gamma_{\text{exit}} = \{L\}$. Then the problem reduces to:

$$\begin{aligned} \psi'' &= 0 \\ \psi'(0) &= 0 \\ \psi(l) &= 0 \\ \psi(L) &= 1 \end{aligned}$$

whose easily obtained solution is the same $\psi(x)$ as in equation 7.

8 Single catalyst particle systems in dimension 2

We explore in this section the behavior of a single catalyst particle system by numerical experiments based on the third boundary value problem (large k approximation). Recall that the problem is to find the harmonic function $\psi(\mathbf{x})$ (i.e., the function satisfying $\nabla^2\psi = 0$) with the boundary conditions described in section A.3. This was done in the examples described below by a standard adaptive finite elements method and implemented in Matlab. Meshes for the finite element procedure were refined up to the point where the error, as measured by the energy norm of the approximation was less than 0.001. A more detailed and systematic study in dimension three that can be used for quantitative comparison with actual TAP experiments will be pursued in another paper.

Consider the system shown in figure 6.

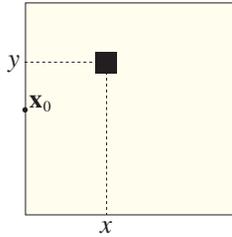


Figure 6: A square catalyst particle of side length 0.1 in \mathcal{R} with center at (x, y) . The point \mathbf{x}_0 is the typical position vector for gas injection into \mathcal{R} , unless otherwise specified.

Figure 7 is the graph of $\alpha(x, y)$, where (x, y) is the current position of a molecule of type A . Thus $\alpha(x, y)$ is the probability that a type A molecule at position (x, y) will undergo reaction before leaving the reactor. The square base on the xy -plane represents the reactor. The exit boundary is the side parallel to the y -axis where the graph touches the xy -plane; i.e., where $\alpha = 0$. The catalyst is on the xy -plane, hidden by the graph, but its position is clearly indicated by the part of the graph that attains value $\alpha = 1$.

Naturally, conversion decreases as the position of a not yet converted A -molecule approaches the exit since it is likely to leave the reactor before hitting the catalyst; and it increases to 1 for A -molecules that are very close to the catalyst.

8.1 Catalyst position and conversion

We now consider how conversion changes as we vary the position of the catalyst particle of the system of figure 6. Later in the paper we compare the qualitative results derived from these computations with experimental measurements in TAP systems. It is not our intension in this paper to make precise numerical predictions about these experiments. This will require solving the above boundary value problems for more realistic geometries. Our goal in numerically exploring simple reactor and catalyst shapes in dimension two is to derive qualitative information that will help plan further experiments.

Let α be the value of conversion with initial point given by the midpoint of the left-hand side of the square reactor shown in figure 6. (The initial point is represented by \mathbf{x}_0 in the figure.) The result is summarized in figure 8. Conversion is greatest when the catalyst is right in front of the initial point and declines as it is moved farther away; as a function of y for any given x , conversion is maximum on the axis of the reactor (running from the mid-left to mid-right sides of the square reactor of figure 6) and decreases as the catalyst is moved away from the center axis towards the upper or lower walls.

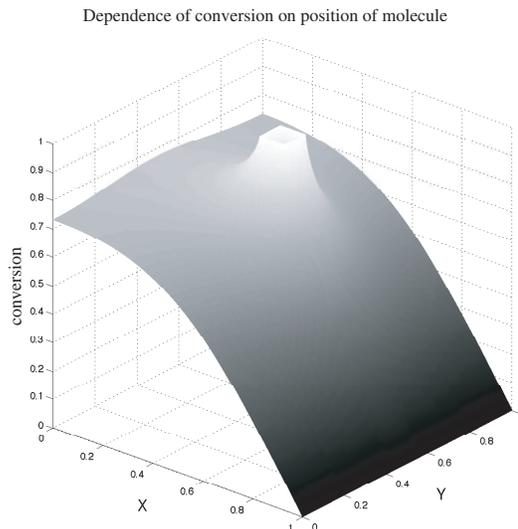


Figure 7: Conversion probability as function of the position in \mathcal{R} . The value $\alpha(x, y)$ is interpreted as the probability that of a single molecule of type A currently at (x, y) will undergo a reaction before leaving the reactor. The geometry is as shown in figure 6. Here, the square sample is at the middle point of the square reactor.

9 Experimental results

The dependence of conversion on catalyst position along the axis of the reactor has been studied experimentally using a TAP reactor system. In this section we describe the experimental approach and compare the experimental results with the theoretical results of section 8.1.

9.1 Single particle TAP pulse response experiment

The catalyst used in the single particle experiments is a circular platinum (Pt) foil with diameter 0.125 in (0.317 cm) and a thickness of 0.004 in (0.01 cm). The Pt foil is surrounded by inert quartz particles with diameters between 210 – 250 μm . The catalyst was placed in three different positions inside the reactor: at the very top, located near the reactor inlet; in the middle; and at the bottom of the reactor close to the outlet. The Pt foil was placed in the reactor with the flat circular surfaces facing the reactor inlet and outlet. The radius of the Pt foil is approximately 0.496 of the radius of the reactor. Similar experiments were performed with Pf foil of smaller size and of square shape.

The reaction used in the single particle Pt foil experiment is CO oxidation, which was chosen because Pt is known to have high activity for such reaction. Also CO oxidation is a model reaction to demonstrate conversion for the irreversible reaction of reactant A (CO) to produce product B (CO_2). If the reaction is fast enough, i.e., for high k values, the boundary value problem 4 can be applied. Thus for the purpose of relating the above theory to experimental data, CO oxidation is an ideal reaction.

In preparation to the TAP pulse response experiment, the Pt foil was pretreated with a continuous O_2/Ar flow (20 cc/min for each gas, $P = 1$ atm, $\text{O}_2/\text{Ar} = 1$) for 1 hr at 375°C to ensure maximum oxygen adsorption on the Pt foil surface. After pretreatment, the slide valve was opened, evacuating

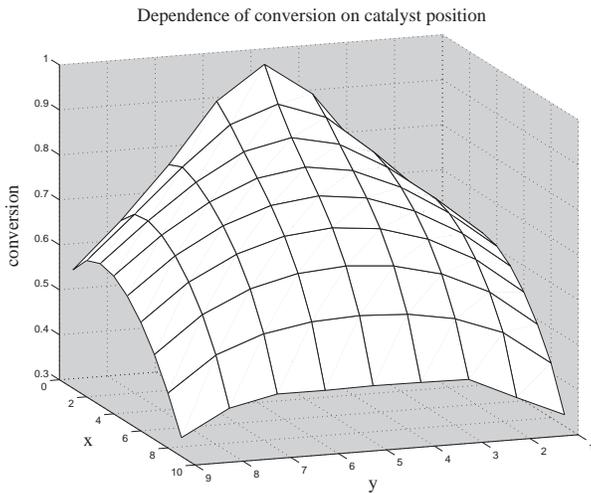


Figure 8: Conversion as function of the center of square catalyst for the situation described in figure 6. The initial position of the gas molecules has coordinates $x = 0$, $y = 1/2$.

the reactor and configuring the system for the experiments. The reactor temperature was maintained at 375°C during the course of the experiments to ensure a fast reaction rate. A series of CO/Ar pulses (CO/Ar = 70/30 feed ratio) were injected into the reactor and CO conversion to CO_2 was measured using the mass spectrometer. Each pulse contains approximately 10^{14} molecules. Ar is always used in the reactant feed blend because it serves as an inert reference to the behavior of the reactants and products. Because Ar is inert, its transient response only depends on the transport process, thus it can be used as a measuring stick for gas diffusivities, conversion, kinetic parameters, and experimental stability, which can be affected by variations in pulse valve intensity during the course of the experiment. Taking the areas under the pulse response curves is equivalent to finding the zeroth moment of the gas outflow [Shek1]. The zeroth moment is useful in TAP data analysis because it is proportional to the amount of molecules of gas exiting the reactor per pulse. Moment analysis is needed to find reactant conversion and product yields.

9.2 Results

The zeroth moment measures the amount of gas coming out of the reactor. At the beginning of the experiment, when the first CO pulses are injected into the reactor, the CO conversion is high because there is more available surface oxygen on the Pt foil. Recall that the Pt foil was first pre-oxidized by an atmospheric oxygen flow. As more CO pulses are introduced into the reactor, there is less and less surface oxygen because it is being used up during reaction with CO to produce CO_2 . At around 750 pulses the CO zeroth moment reaches a flat plateau indicating no more conversion of CO. The behavior of CO_2 is the exact opposite. Initially, zeroth moment, or production, of CO_2 is at a maximum because the CO injected into the reactor has a greater chance of finding oxygen to react with as there is more of it available on the catalyst surface. As more pulses of CO are injected into the reactor, the surface oxygen is depleted away, diminishing CO_2 production.

The Pt foil was placed in three different positions inside the reactor: top (near the reactor entrance), middle, and bottom. The CO_2 yield, or the CO conversion, is shown in figure 9. The yield is obtained by taking an average of the first 10 CO pulses, because this is the range of maximum

conversion when the catalyst was at a completely oxidized state. The x -axis of the graph on figure 9 gives the Pt foil position within the reactor. Position 0 on figure 9 represents the reactor inlet and position 1 represents the reactor outlet. The experimental data are represented in the figure by the three rectangular boxes. The center of each rectangle gives the point estimate of yield for the respective position; the height of the rectangle is twice the standard deviation of the measured yield, and the width of the rectangle is a rough estimation of the uncertainty in placing the Pt foil in the reactor.

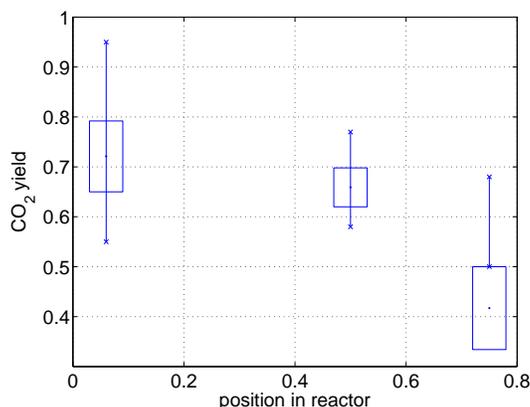


Figure 9: CO_2 yield/ CO conversion of single 0.125 in diameter Pt foil at 3 different locations in the reactor at 375°C . Position 0 indicates the reactor entrance and position 1 the reactor outlet. The rectangular boxes describe the experimentally obtained values for the yield, and the vertical line segments the theoretical values as explained in the text.

The theoretical values obtained by solving numerically boundary value problem 4 (section 8) are represented in the same graph by the vertical line segments. The segment gives the range of values, for a fixed position x along the length of the reactor, for all the values of y from the lower to the upper reactor wall. See figure 10 for a more detailed description of this range for the midpoint foil position $x = 0.5$.

CO conversion is greatest when the Pt foil is placed near the reactor entrance due to the transport properties of the CO molecules in the reactor. In the Knudsen diffusion regime the diffusivity of each gas in a mixture is independent of the composition of the mixture [Gle2]. When the Pt foil is placed near the reactor entrance, there is a greater probability for CO molecules to keep returning near the catalyst particle due to the random (Brownian) motion caused by the multiple collisions with the inert particles in the reactor bed. As the Pt foil is moved closer to the reactor outlet the probability that a CO molecule will come back and hit the catalyst foil once it has passed the position where the catalyst is located decreases. Notice that the nature of the random motion is important for explaining both the relatively high yield for a single catalyst particle and the way the yield depends on the catalyst position: random motion creates the opportunity for the molecule to return multiple times to where the catalyst is located, but the number of returns decreases if the distance between the position of the Pt foil and the reactor outlet decreases. Once a molecule reaches the reactor outlet, it exits the reactor into the vacuum chamber.

Figure 10 shows the numerical values for conversion for $x = 0.5$ and y between 0 and 1. The range of conversions for $x = 0.5$ and $0 < y < 1$ is between 58% and 77%. This is compared with the experimental result 68%.

The qualitative result of decreasing yield with catalyst position is in agreement with what was obtained numerically. The values for conversion shown in figure 9 also seem to be in reasonably good agreement with the numerical values obtained earlier (see figure 8) for the idealized TAP experiment on a square, with a square catalyst. Despite the rather idealized nature of the two dimensional model, the experimental values fall within the range of theoretical values for the first two points, nearer to the reactor inlet. Greater discrepancy is seen near the reactor outlet, indicating that gas molecules near the exit tend to leave somewhat sooner than expected by the theoretical model. It is possible that near that end the Brownian motion approximation is not as good as it is deeper inside the reactor as the granular nature of the medium begins to show itself. It is also possible that the simple square reactor model does not serve equally well near the border of transition into the vacuum chamber and a more realistic reactor shape is needed. It is important to emphasize, however, that a careful quantitative comparison between theory and experiment cannot be done on the basis of two dimensional numerical experiments, mainly because Brownian motion in dimension 2 is known to differ in important ways from Brownian motion in dimension 3. For example, Brownian motion in 3-space is transient whereas in 2-space it is recurrent [Øks]. This suggests that conversion in dimension 3 should be less than in dimension 2 for comparable configurations of catalyst size and position. Also, it is not clear how to compare catalyst size in dimensions 2 and 3. For the square reactor model, the width of the catalyst particle is 1/10 of the width of the reactor, whereas the area of the Pt foil is approximately 1/4 of the cross sectional area of the reactor. (In terms of “area” ratios, where “area” in dimension two is taken to be the length of the catalyst surface, the two numbers are 2/5 and 1/2.) It is possible that a reduction in yield due to dimension somewhat compensates for the higher cross-section ratio in the actual experiment, and the relatively good numerical agreement for the first two positions in figure 9 (or the relative disagreement of the third) is accidental. Therefore, meaningful quantitative comparisons will have to wait for a numerical study of more realistic reactor-catalyst configurations, which we plan to do in a future paper.

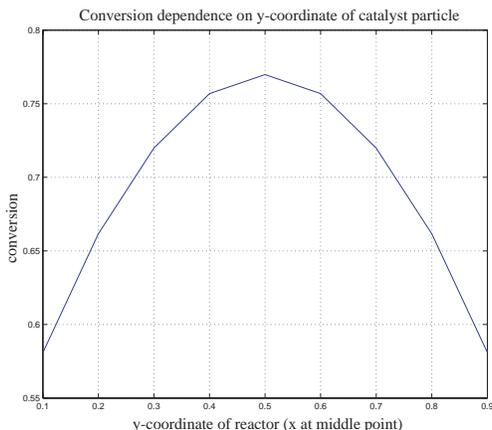


Figure 10: Conversion for $x = 0.5$ (middle point along axis) and variable y , given in multiples of step size 0.1.

10 Numerical experiments for two-particle systems

The TAP experiments performed so far have been done for single catalyst particle systems. We have done a small number of numerical experiments involving two-particle systems. They reveal an interesting effect suggesting that maximal conversion happens when the particles are at an optimal distance from each other. We plan to test this observation in future experiments.

Each catalyst particle is a line segment of length 0.2 placed in a square reactor of side length 1. We consider two configurations: in the first, the particles are aligned with the main axis of the reactor, one fixed at the midpoint and the other is moved along the axis. In the second configuration the particles are similarly moved but on the axis connecting top and bottom walls in the middle of the reactor.

10.1 Parallel catalyst pair along the reactor axis

Consider now the configuration of figure 11. A pair of straight line catalysts, perpendicular to the axis of the reactor, are placed at a distance of each other, and we wish to investigate how conversion changes as a function of that distance. Specifically, one of the catalysts is placed at the middle position and the position of the second varies along the axis.

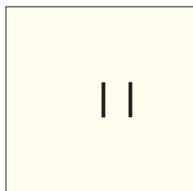


Figure 11: A vertical catalyst pair. As their distance decreases, conversion approaches the value of a single line.

Figure 12 shows the dependence of conversion on the position of both catalyst particles, as given by the distance from each to the back side of the reactor. The most important feature of the graph is that, as the two particles come close together conversion decreases to the value that would be obtained for a single particle. At the minimum for α in figure 13, conversion has the same value as at the corresponding position, $x = 0.5$, for a single particle. (The corresponding one-particle graph is not shown.)

Figure 13 gives the dependence of conversion on position of the second catalyst sample along the reactor axis when the first catalyst sample is placed at the middle point, $x = 0.5$. The graph suggests that a system with multiple catalyst particles achieves maximal efficiency of conversion when the catalyst particles are separated by very specific distances. When they come closer together than that optimal value, conversion sharply decreases to that of a single particle. This optimal distance is apparent on the part of the graph of figure 13 for y (position of second catalyst particle) over the interval between 0.5 and 0.9. (For $y < 0.5$ we simply see the monotone increase to 1 as y goes to 0 due to one sample approaching the point where gas enters the reactor.) This same phenomenon is also observed in the next experiment.

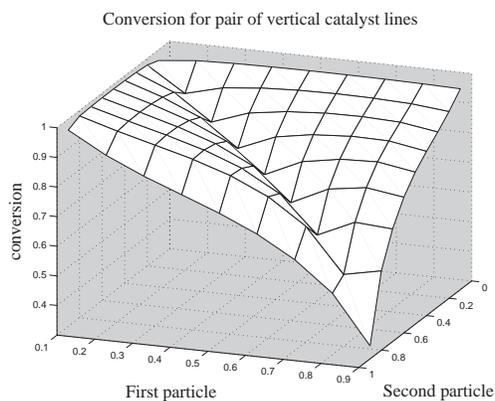


Figure 12: Pair of vertical catalyst particles. Coordinates (x, y) represent one line particle a distance x from the back side, and the other at distance y , both centered along the reactor axis.

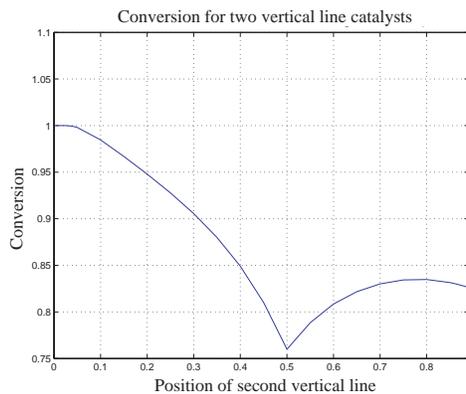


Figure 13: Slice of the graph of figure 12 corresponding to $x = 0.5$ (or $y = 0.5$, since that graph is symmetric). When y is between 0.5 and 1 varies from approximately 0.75 (the value for a single particle at the center of the reactor) to a maximum of approximately 0.85 for $y = 0.77$, then decreases again to less than 0.8 when $y = 1$. (The graph only shows conversion for y between 0 and 1, but note that, past $y = 1$, the second catalyst becomes ineffective and conversion should drop to approximately 0.75.)

10.2 Catalyst pair along a perpendicular line to reactor axis

This is similar to the previous experiment except that the catalyst samples are horizontal line segments placed at different heights at the center of the reactor.

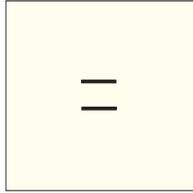


Figure 14: A sample pair placed along the middle line perpendicular to the reactor axis. The position of both line segments is allowed to vary.

The graph of figure 15 shows that maximal conversion happens when the samples lie approximately 0.3 apart, symmetrically relative to the reactor axis. Together with the previous experiment (figures 12 and 13) this points to the general principle that efficiency of conversion that one would hope to gain by adding several catalyst samples would be severely compromised by the need to bring them too close together. A more detailed numerical expression of this observation will be investigated later.

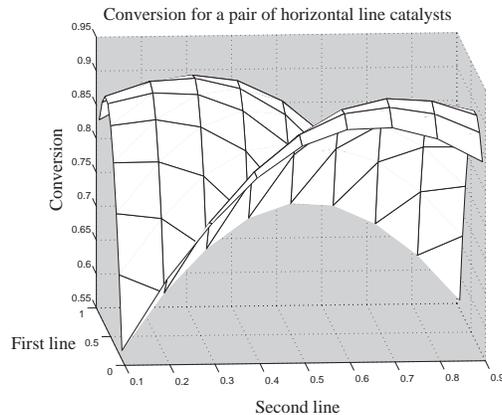


Figure 15: Conversion as a function of the heights of both catalyst samples.

11 Conclusions

- This paper implements the beginning of a general theory of reaction and diffusion for Temporal Analysis of Products (TAP) systems based on a probabilistic approach. Using the mathematical theory of random processes with killing and the Feynman-Kac formula we have shown that conversion for the irreducible reaction $A \rightarrow B$ over a general distribution of catalyst in a TAP reactor can be obtained by solving a time independent boundary value problem (BVP). The main advantage of this approach is that it applies to general spatial catalytic configurations.
- A number of versions of this BVP were also obtained which apply to several useful special cases. In particular, we obtain a very simple derivation of the value of conversion for thin-zone TAP systems. Our method also applies in a straightforward way to much more general catalyst configurations.
- Using another special form of our general BVP we study a single-particle TAP system and the dependence of conversion on the position of the catalyst particle in the reactor. This study is done first numerically, by solving the BVP for a range of positions of the catalyst, and also experimentally. Although we have used a very simplified, 2-dimensional model of the TAP reactor, calculation and experiment give the same qualitative behavior and a comparable range of values.
- We have also studied 2-particle TAP systems numerically and investigate how conversion depends on the catalyst particles configuration. The preliminary results show the following interesting effect: There seems to be an optimal distance between the two particles that produces maximum yield.

In a future paper we will solve the BVP for a realistic TAP-reactor geometry and will study in a more systematic way multi-particle catalyst configurations. We are also planning experiments for multi-particle TAP systems.

Another development that will be pursued later is the study of more general reactions. In addition to the probability of adsorption to a catalyst particle (the main theoretical concept of this paper), a theory for general reaction mechanisms requires knowledge of expected times to adsorption, conditional on adsorption taking place. It turns out that such time parameters can be obtained via boundary value problems that are similar to the ones studied in this paper.

A Explanation of the results of section 6

We give here a brief, non-technical explanation for the conclusions of section 6 stating that the survival function ψ must satisfy the given boundary value problems.

A.1 Killing process and the Feynman-Kac formula

In this section we provide some explanations for the results of section 6. The main theoretical idea we explore is that the diffusion-reaction process for gas A can be described by a stochastic process known as *diffusion with killing*.

We take a moment to describe the general idea before concentrating on the particular situation at hand. Let $V(\mathbf{x})$ be a function defined on a region \mathcal{R} , which we refer to as the *potential*. Denote by H the operator on functions defined by

$$H\psi = -\frac{1}{2}\sigma^2\nabla^2\psi + V(\mathbf{x})\psi.$$

(Functional analytic issues about domains of operators, which are necessary for a proper mathematical analysis, will be ignored here. The reader should consult, for example, [Simon] or [Øks], for the finer mathematical points that we will not deal with here.) We wish to obtain a probabilistic description of the solution $\psi(\mathbf{x}, t)$ of the equation

$$\frac{\partial \psi}{\partial t} = -H\psi. \quad (8)$$

Note that the similar looking equation $\frac{\partial \psi}{\partial t} = -iH\psi$ is the Schrödinger equation with potential $V(\mathbf{x})$ (and Planck constant set to 1). In our case, $V(\mathbf{x}) = k\eta(\mathbf{x})$, $\sigma^2 = 2D$, η is the catalyst distribution introduced earlier in the paper, and k is the reaction constant for the $A \rightarrow B$ reaction. It is traditional in probability theory to interpret this irreversible reaction as “killing” A .

The solution $\psi(\mathbf{x}, t)$ of equation 8 has the following probabilistic interpretation. We regard $V(\mathbf{x})$ as the *killing rate* at \mathbf{x} of molecules that undergo random motion described by X_t (see equation 5), starting at \mathbf{x} at time 0. Suppose that we wish to obtain the average value of $g(X_t)$, where g is a given function. Define $\psi(\mathbf{x}, t)$ as the expectation of $g(X_t)$, i.e., the expected value of g at the random position of the molecule at time t *provided* that the molecule has not been killed by time t . (If it has, we set $g(X_t) = 0$.) The initial condition for ψ is naturally $\psi(\mathbf{x}, 0) = g(\mathbf{x})$ and the solution of 8 has the operator expression

$$\psi(\mathbf{x}, t) = (e^{-tH}g)(\mathbf{x}).$$

The Feynman-Kac formula expresses this solution by the formula shown in the next theorem.

Theorem A.1 (The Feynman-Kac formula) *The solution of the diffusion with killing equation 8 and initial condition $\psi(\mathbf{x}, 0) = g(\mathbf{x})$, is given by*

$$(e^{-tH}g)(\mathbf{x}) = E^{\mathbf{x}} \left[e^{-\int_0^t V(X_s) ds} g(X_t) \right].$$

Here $E^{\mathbf{x}}$ denotes conditional probability given that $X_0 = \mathbf{x}$. This formula says that the solution $\psi(\mathbf{x}, t)$ is obtained by letting the molecule (of type A) diffuse according to the process of equation 5, but with a chance to vanish from its current position (turn to B) at a rate proportional to the value of V at that position. The exponential factor is the probability that the molecule has not yet been killed at time t .

Before returning to the specific case at hand, we note that if $\psi(\mathbf{x})$ is time-independent and solves the equation $H\psi = 0$, then

$$\psi(\mathbf{x}) = (e^{-tH}\psi)(\mathbf{x})$$

for all $t \geq 0$. Applying the Feynman-Kac formula to this case gives that a solution to $H\psi = 0$ must satisfy the equation

$$\psi(\mathbf{x}) = E^{\mathbf{x}} \left[e^{-\int_0^t V(X_s) ds} \psi(X_t) \right] \quad (9)$$

for all $t \geq 0$. We now choose t in this expression to be the random time, denoted T , at which X_t reaches the exit boundary, Γ_{exit} . We also assume that ψ equals 1 on Γ_{exit} and that X_t reflects without killing at all other boundary components of \mathcal{R} . Thus ψ satisfies $\psi(X_T) = 1$ and the Neumann boundary condition on $\Gamma_{\mathcal{R}}$ and $\Gamma_{\mathcal{S}}$: $\mathbf{n} \cdot \nabla \psi = 0$. This leads to the following result:

Theorem A.2 *The solution $\psi(\mathbf{x})$ to the boundary value problem:*

$$\begin{aligned} H\psi &= 0 \text{ on } \mathcal{R} \\ \psi &= 1 \text{ on } \Gamma_{\text{exit}} \\ \mathbf{n} \cdot \nabla \psi &= 0 \text{ on } \Gamma_{\mathcal{R}} \cup \Gamma_{\mathcal{S}} \end{aligned}$$

is given by

$$\psi(\mathbf{x}) = E^{\mathbf{x}} \left[e^{-\int_0^T V(X_s) ds} \right],$$

where T is the first passage time to Γ_{exit} .

The main result of section 6 (first boundary value problem) is an immediate consequence of theorem A.1 and the discussion and definitions of section 3.

A.2 Second boundary value problem

We indicate now how the boundary value problem 2 is obtained from the more general problem 1. The thickness δ of the active zone around the catalyst particle is now assumed to be very small compared to the size of the particle. Thus we think of the active zone as a very thin skin over the surface of the catalyst.

The rectangular slab shown in figure 16 represents a small element of this active skin, placed on top of the catalyst surface. We denote this element by V . The catalyst surface is indicated in the figure by the larger square in dashed lines. The surface boundary of V is represented by S . It consists of a top square side facing the interior of the reactor, a bottom square side sitting right atop the surface of the catalyst, and four lateral rectangular sides.

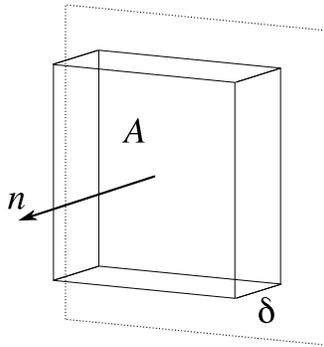


Figure 16: The rectangular slab describes a small element of active region. It has thickness δ and top surface area A . The unit normal vector pointing into the reactor and against the surface of the catalyst is indicated by \mathbf{n} .

The gradient $\nabla\psi$ is normal to the catalyst surface, so its integral over the boundary surface S is given approximately by

$$\int_S \mathbf{n} \cdot \nabla\psi dS = A \langle \mathbf{n} \cdot \nabla\psi \rangle,$$

where the angle brackets indicate average value over that small surface area. (Notice that on the 4 lateral faces and the back-face of the volume element the normal derivative of ψ vanishes.)

The divergence theorem expresses this quantity as the volume integral of the Laplacian of ψ over V . This Laplacian is equal to $\eta k\psi/D$, and $\eta = 1$ in the active region. Thus

$$A \langle \mathbf{n} \cdot \nabla\psi \rangle = \int_V (k\psi/D) dV = A\delta k \langle \psi \rangle / D.$$

The angle brackets on the right-hand side of the equation denote average over V . Now, supposing that ψ and its first derivative in space are continuous and that the volume element V is very small,

we replace the indicated average values with ψ and $\mathbf{n} \cdot \nabla \psi$ near the surface of the catalyst, $\Gamma_{\mathcal{S}}$. The result is that the relation

$$\mathbf{n} \cdot \nabla \psi - \frac{\delta k}{D} \psi = 0 \quad \text{on } \Gamma_{\mathcal{S}}$$

holds, as was claimed in section 6.

A.3 Limit of high k and harmonic functions

For many reactions the value of the constant k is high. It is, therefore, of interest to consider the limit case of $k = \infty$. This means that a reaction event $A \rightarrow B$ necessarily occurs as soon as a gas molecule enters the active zone. If the active zone around the surface of the catalyst is very thin, then we can assume that a reaction event necessarily takes place when a molecule of type A collides with that surface.

In this case we no longer need to specify the function η . If the point \mathbf{x} is very close to the surface of \mathcal{S} , then the probability of non-conversion approaches 0, and away from that surface we can assume that $\eta = 0$, so the probability $\psi(\mathbf{x})$ given by the expression A.1 can now be interpreted as the probability that a molecule of type A , initially at \mathbf{x} , will not collide with the sample before leaving the reactor. In this case, the boundary value problem of theorem A.2 reduces to the one of the next theorem.

This is a special case of the well-known result about the interplay between probability theory and harmonic functions, first studied Kakutani in the 1940s. The general observation is as follows. Let \mathcal{R} be a region in \mathbb{R}^n which is bounded in the sense that it is entirely contained within a finite radius of some point. Let Γ be the boundary of \mathcal{R} , which is the union of an absorbing boundary Γ_a and a reflecting boundary Γ_r . Let g be a function on Γ_a . Then the function ψ on \mathcal{R} such that $\nabla^2 \psi = 0$, with $\psi = g$ on Γ_a and $\mathbf{n} \cdot \nabla \psi = 0$ on Γ_r , is

$$\psi(\mathbf{x}) = E^{\mathbf{x}}[g(B_T)],$$

where B_t denotes Brownian motion in \mathcal{R} starting at \mathbf{x} at $t = 0$ and T is the random time at which B_t first reaches Γ_a .

To calculate conversion for high k values, we assume that the absorbing boundary Γ_a is the union of two components: Γ_{exit} and $\Gamma_{\mathcal{S}}$ as defined earlier, and set g to be 1 at Γ_{exit} and 0 at $\Gamma_{\mathcal{S}}$. Then the expected value $E^{\mathbf{x}}[g(B_T)]$ is naturally interpreted as the probability of leaving the region \mathcal{R} without first hitting the boundary of \mathcal{S} . In the limit $k = \infty$ the event of hitting \mathcal{S} is equivalent to the event of conversion $A \rightarrow B$, so $\psi(\mathbf{x})$ is the probability that an A -molecule initially at \mathbf{x} will not react before leaving \mathcal{R} . Notice that the result no longer depends on the value of the diffusion constant D . Changing the diffusion constant only rescales the time coordinate without affecting the spacial distribution of the random paths.

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