# Some Properties of the A + B → C Reaction-Diffusion System with Initially Separated Components

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We study some properties of the A + B → C reaction-diffusion system with initially separated components, first analyzed by means of an asymptotic scaling argument by Gálfi and Rácz. We show that, in contrast to the asymptotic result that predicts that the rate of production of C goes like $t^{-1/2}$, at early times it is shown to increase as $t^{1/2}$. Deviations from this behavior appear at times inversely proportional to the reaction constant. Analogous crossover properties appear in the kinetic behavior of the reaction front. A second part of the study is concerned with the same chemical reaction on a fractal surface. When the substrate is a percolation cluster at criticality, both the maximum production rate and the width of the reaction zone differ considerably from those for the homogeneous space.

**KEY WORDS:** Reaction-diffusion equation; exact enumeration method; percolation system; fractal medium.

## 1. INTRODUCTION

The kinetic behavior of diffusion-controlled reactions has stimulated an enormous amount of research since the initial seminal investigation by Smoluchowski.[1,2] However, only within the last 20 years has a part of this research been focused on the phenomenon of self-segregation of reactants in reactions taking place in low numbers of dimensions.[3-7] Most theoretical investigations of such reactions are based on the assumption that the reactants are initially uniformly mixed. It is, however, difficult to implement such conditions in a real chemical system. A simpler system lending

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itself more readily to experimental study is one in which the reactants are initially separated.[8] In that case, one can expect to find phenomena exemplified by an interface or front that separates the reactants and persists in time, the characteristics of the interface depending on whether the reaction rate is finite or infinite. The presence of a reaction front is a characteristic of a variety of biological, chemical, and physical processes.[9–15] An initial step in elucidating the kinetics of pattern formation in such systems consists in understanding the kinetics of simplified models which also exhibit such phenomena.

The first investigation of properties of such a system, the reaction $A + B \rightarrow C$, that takes into account an initial separation of reactants, as opposed to a uniform mixture, appears to be due to Gálfi and Rácz.[16] They developed a theory based on the assumption that the reaction-diffusion equations describing the kinetics of the reaction have a solution approaching an asymptotic scaling form. Analysis of the implications of such a scaling form leads to specific predictions for the exponents appearing in the solution, which have been confirmed in a number of experimental systems.[8,17] For example, Koo *et al.*[17] have verified that the reaction rate is proportional to $t^{-1/2}$ at sufficiently long times, in accordance with the prediction of Gálfi and Rácz.

In the present paper we examine a number of further aspects of the reaction studied by Gálfi and Rácz. In particular, we show, using a perturbation analysis based on letting a suitable dimensionless reaction rate tend toward zero, that at short times the reaction rate increases at a rate proportional to $t^{1/2}$, followed by a crossover to the predicted $t^{-1/2}$ behavior at sufficiently long times. Other novel crossovers in the kinetics are also possible at very short times, as can be determined by the perturbation technique. We confirm by the method of exact enumeration that the exponents predicted by Gálfi and Rácz show up at a reasonable time, which is to say that the scaling regime does not occur at a time so large as to render it physically unobservable. Gálfi and Rácz scaling analysis was carried out for the special case in which the diffusion coefficients of the A and B species are equal. Since their analysis presumes that a reaction-diffusion equation describes the kinetics of the reaction, it does not take into account fluctuations in concentration. More recently, Jiang and Ebner[18] simulated a very similar system, replacing the diffusion process by a random walk on a two-dimensional lattice, with the A and B reactants initially separated by a line. Their simulations showed that the asymptotic scaling assumptions of Gálfi and Rácz remain valid even when the initial densities and diffusion constants are unequal.

Finally, the Gálfi–Rácz analysis assumes that diffusion occurs in a translationally-invariant medium. We examine some of the implications of

having the reactions occur on a fractal substrate, finding the appropriate exponents by a combination of scaling arguments and simulations based on the method of exact enumeration.[19,21]

## 2. THE TRANSLATIONALLY-INVARIANT SUBSTRATE

As a first step in our analysis, we consider a reaction-diffusion system, $A + B \xrightarrow{k} C$, for which the kinetic equations obeyed by the local concentrations $\rho_a$ and $\rho_b$ are those studied by Gálfi and Rácz:

$$\frac{\partial \rho_a}{\partial t} = D_a \nabla^2 \rho_a - k \rho_a \rho_b \tag{1a}$$

$$\frac{\partial \rho_b}{\partial t} = D_b \nabla^2 \rho_b - k \rho_a \rho_b \tag{1b}$$

assuming a mean field approach. Equations (1a) and (1b) are to be solved subject to the initial conditions

$$\rho_a(x, 0) = a_0 H(x), \qquad \rho_b(x, 0) = b_0 [1 - H(x)] \tag{2}$$

in which $H(x)$ is a Heaviside step function, and $a_0$ and $b_0$ are the initial concentrations. That is to say, the reactants are initially separated, the A species being uniformly distributed on the right-hand side, and the B species uniformly distributed on the left side. Our calculations are carried out under the assumption that the system is infinite in either direction. In order to study the short-time behavior of the solution to this set of equations, we develop a perturbation series based on the idea that reactive effects are small relative to diffusive effects, in a suitably dimensionless form.

The system of equations in (1a) and (1b) will be reparametrized in terms of the initial concentrations by setting

$$\rho_a(x, t) = a_0 \alpha(x, t), \qquad \rho_b(x, t) = b_0 \beta(x, t) \tag{3}$$

where $\alpha$ and $\beta$ are now dimensionless concentrations. Two dimensionless constants will be defined in terms of the diffusion constants and the initial concentrations. These are

$$\mathscr{D} = \left(\frac{D_a}{D_b}\right)^{1/2}, \qquad r \equiv \left(\frac{a_0}{b_0}\right)^{1/2} \tag{4}$$

both of which we take to be $O(1)$. At sufficiently early times, the amount of mixing of A and B molecules will not be very great; consequently, the

amount of the product C will necessarily be small. We can simulate this early-time behavior over a longer interval of time by letting the reaction rate go to zero in a suitable dimensionless sense. The dimensionless small parameter in our problem will be denoted by $\varepsilon$, which is defined by

$$\varepsilon = \frac{k}{(a_0 b_0 D_a D_b)^{1/2}} \tag{5}$$

Finally, we introduce a dimensionless time $\tau$ and a dimensionless space variable $\xi$ by

$$\tau = t a_0 b_0 (D_a D_b)^{1/2}, \qquad \xi = x (a_0 b_0)^{1/2} \tag{6}$$

Equations (1) can be rewritten in terms of the variables defined in Eqs. (3)–(6) as

$$\frac{\partial \alpha}{\partial \tau} = \mathscr{D} \frac{\partial^2 \alpha}{\partial \xi^2} - \frac{\varepsilon}{r} \alpha \beta \tag{7a}$$

$$\frac{\partial \beta}{\partial \tau} = \frac{1}{\mathscr{D}} \frac{\partial^2 \beta}{\partial \xi^2} - \varepsilon r \alpha \beta \tag{7b}$$

These equations are the starting point for a straightforward application of perturbation theory on the assumption that $\varepsilon \ll 1$. We expand $\alpha$ and $\beta$ into the series

$$\alpha = \sum_{j=0}^{\infty} \alpha_j \varepsilon^j, \qquad \beta = \sum_{j=0}^{\infty} \beta_j \varepsilon^j \tag{8}$$

finding that $\alpha_0$ and $\beta_0$ satisfy ordinary diffusion equations that must be solved subject to the initial conditions $\alpha_0(\xi, 0) = H(\xi)$, $\beta_0(\xi, 0) = 1 - H(\xi)$. The solution to these equations that satisfies the given initial conditions is

$$\alpha_0(\xi, \tau) = \Phi\left(\frac{\xi}{(2\mathscr{D}\tau)^{1/2}}\right), \qquad \beta_0(\xi, \tau) = 1 - \Phi\left(\xi \left(\frac{\mathscr{D}}{2\tau}\right)^{1/2}\right) \tag{9}$$

in which $\Phi(z)$ is the normal integral defined by

$$\Phi(z) = \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{z} e^{-u^2/2} \, du \tag{10}$$

We follow Gálfi and Rácz in defining the *local* rate at which C is produced at position $x$ and time $t$ as $R(x, t) = k \rho_a(x, t) \rho_b(x, t)$, with the implied *global* rate of production of C:

$$R(t) = k \int_{-\infty}^{\infty} \rho_a(x, t) \rho_b(x, t) \, dx$$

$$= a_0 b_0 (D_a D_b)^{1/2} \varepsilon \int_{-\infty}^{\infty} \alpha(\xi, \tau) \beta(\xi, \tau) \, d\xi \tag{11}$$

The local rate of production of C can obviously also be expanded in a series that goes in powers of $\varepsilon$. Useful information on the early-time behavior of the global reaction rate can then be obtained from the lowest order of perturbation theory, in which the integrand of Eq. (11) is replaced by $h_0(\xi, \tau) \equiv \alpha_0(\xi, \tau) \beta_0(\xi, \tau)$. We will expand the dimensionless reaction rate, now regarded as a function of $\tau$, $R(\tau)$, in a perturbation series in the small parameter $\varepsilon$:

$$R(\tau) = a_0 b_0 (D_a D_b)^{1/2} \varepsilon [\mathscr{R}_0(\tau) + \varepsilon \mathscr{R}_1(\tau) + \cdots] \tag{12}$$

The lowest order term in the expansion in Eq. (12) is readily found to be

$$\mathscr{R}_0(\tau) = \int_{-\infty}^{\infty} h_0(\xi, \tau) \, d\xi = C_0 \sqrt{\tau} \tag{13}$$

where $C_0$ is the constant

$$C_0 = \int_{-\infty}^{\infty} \Phi\left(\frac{v}{(2\mathscr{D})^{1/2}}\right) \left[1 - \Phi\left(v\left(\frac{\mathscr{D}}{2}\right)^{1/2}\right)\right] dv \tag{14}$$

Thus, there is a crossover from the early-time behavior of the reaction rate which increases proportional to $\tau^{1/2}$ to the asymptotic $\tau^{-1/2}$ behavior predicted by the scaling theory of Gálfi and Rácz.

Having obtained the lowest order approximation to the overall reaction rate, we next inquire as to the range in time for which we expect this approximation to be valid. For this purpose we first calculate the first-order correction in the perturbation expansion in Eq. (8). The equation satisfied, for example, by $\alpha_1(\xi, \tau)$ is

$$\frac{\partial \alpha_1}{\partial \tau} = \mathscr{D} \frac{\partial^2 \alpha_1}{\partial \xi^2} - \frac{1}{r} h_0(\xi, \tau) \tag{15}$$

whose solution can be found in terms of the Green's function for the diffusion equation. The result can be expressed in terms of a double integral as

$$\alpha_1(\xi, \tau) = -\frac{1}{r(4\pi\mathscr{D})^{1/2}} \int_{-\infty}^{\infty} d\lambda \int_0^{\tau} \frac{d\tau'}{(\tau - \tau')^{1/2}} h_0(\lambda, \tau')$$
$$\times \exp\left\{-\frac{(\xi - \lambda)^2}{4\mathscr{D}(\tau - \tau')}\right\} \tag{16}$$

The solution for $\beta_1(\xi, \tau)$ has the same form, except that $r$ is to be replaced by $1/r$ and $\mathscr{D}$ is to be replaced by $1/\mathscr{D}$. We note first that $h_0(\xi, \tau)$ is a function only of $\xi/\sqrt{\tau}$; specifically,

$$h_0(\xi, \tau) = \Phi\left(\frac{\xi}{(2\mathscr{D}\tau)^{1/2}}\right) \left[1 - \Phi\left(\frac{\xi\sqrt{\mathscr{D}}}{(2\tau)^{1/2}}\right)\right] \equiv f\left(\frac{\xi}{\sqrt{\tau}}\right) \tag{17}$$

where $f(u)$ is defined by the equation. It follows from this observation that $\alpha_1(\xi, \tau)$ can be written in the generic scaling form

$$\alpha_1(\xi, \tau) = -\tau g\left(\frac{\xi}{\sqrt{\tau}}\right) = -\tau g(\rho) \tag{18}$$

where $\rho$ is defined to be $\xi/\sqrt{\tau}$ and the function $g(\rho)$ can be expressed in terms of a double integral. The form of $g(\rho)$ is found from Eq. (16), by changing the variables of integration to $u$ and $\varDelta$, defined by

$$u = \frac{\lambda}{\sqrt{\tau'}}, \qquad \varDelta = \frac{\tau'}{\tau} \tag{19}$$

The Jacobian of this transformation is readily found to equal $\tau^{3/2}\sqrt{\varDelta}$. In terms of the new set of variables the function $\alpha_1(\xi, \tau)$ becomes

$$\alpha_1(\xi, \tau) = -\frac{1}{r(4\pi\mathscr{D})^{1/2}}\tau\int_{-\infty}^{\infty} du \int_0^1 d\varDelta \left(\frac{\varDelta}{1-\varDelta}\right)^{1/2} f(u)$$

$$\times \exp\left\{-\frac{(\rho - u\sqrt{\varDelta})^2}{4\mathscr{D}(1-\varDelta)}\right\} \tag{20}$$

We see that the value of the double integral is a function of $\rho$ only, which, together with the multiplicative factor $\tau$, confirms the scaling behavior shown in Eq. (18). A similar consideration applied to the function $\beta_1(\xi, \tau)$ suffices to show that it also has the same scaling form as that shown in Eq. (18).

We now proceed to calculate the correction to the global reaction rate in Eq. (12). The correction term, $\mathscr{R}_1(\tau)$, is given by

$$\mathscr{R}_1(\tau) = \int_{-\infty}^{\infty} \left[\alpha_0(\xi, \tau)\beta_1(\xi, \tau) + \alpha_1(\xi, \tau)\beta_0(\xi, \tau)\right] d\xi \tag{21}$$

By inserting the scaling form of the different functions that appear in the integrand, one finds the short-time behavior of $\mathscr{R}_1(\tau)$ to be

$$\mathscr{R}_1(\tau) = C_1\tau^{3/2} \tag{22}$$

where $C_1$ is a constant expressible in terms of a double integral that depends not only on $\mathscr{D}$, but also on the ratio of initial reactant concentrations. This first correction enables us to predict the time at which one first can detect deviation from the initial $\tau^{1/2}$ behavior of the reaction rate. As a combination of the fact that $\mathscr{R}_0(\tau)$ is proportional to $\tau^{1/2}$ and the time dependence in Eq. (22), one finds that the deviation occurs at values of the

dimensionless time $\tau_d \sim C_0/(C_1 \varepsilon)$, where these constants are defined in Eqs. (13) and (22). If we make use of the parametrization in Eqs. (5) and (6), we find

$$t_d \sim \frac{C_0}{C_1 k (a_0 b_0)^{1/2}} \tag{23}$$

with the implication that an increase in reactant concentration is equivalent, in effect, to an increase in the rate constant.

We now apply the same type of analysis to study the short-time limit of the kinetic behavior of the reaction front. Let $\xi_f$ be the center of the reaction zone, which is defined as the position at which the local reaction rate is a maximum. To zeroth order in $\varepsilon$, the local reaction rate is given by $h_0(\xi, \tau)$, whose form is shown in Eq. (17). Since it has the scaling behavior indicated there, the lowest order behavior of $\xi_f$ is

$$\xi_f \sim s(2\tau)^{1/2} \tag{24}$$

in which the parameter $s$ is a constant, which can be calculated as that point at which the function

$$f(s) \equiv \Phi \left( \frac{s}{\sqrt{\mathscr{D}}} \right) [1 - \Phi(s \sqrt{\mathscr{D}})] \tag{25}$$

is a maximum. In the special case $D_a = D_b$ or, equivalently, $\mathscr{D} = 1$, one finds that the position of the maximum is specified by $s = 0$, so that the reaction zone center to order $\tau^{1/2}$ remains fixed in position. In that case we must retain the next-order term in the perturbation expansion of the dimensionless local reaction rate $\mathscr{R}(\xi, \tau)$ to determine the short-time behavior of $\xi_f$. We then find that

$$\mathscr{R}(\xi, \tau) \sim f(\rho) + \varepsilon \tau m(\rho) + \cdots \tag{26}$$

where $\tau m(\rho)$ is essentially the integrand of Eq. (21). Since the condition $\mathscr{D} = 1$ implies that to lowest order $\xi_f = 0$, which is valid at the very shortest times, in order to find the behavior of this quantity at slightly longer times, we expand both terms in Eq. (26) around $\rho = 0$, noting that in this limit $g(0) = \text{const}$. On expanding both $\Phi(\rho)$ and $m(\rho)$ in the neighborhood of $\rho = 0$, we find that the lowest order terms in the series for $\mathscr{R}(\xi, \tau)$ are

$$\mathscr{R}(\xi, \tau) \sim \frac{1}{4} - \frac{\xi^2}{4\pi\tau} + \varepsilon\tau \left( m(0) + \frac{\xi}{\sqrt{\tau}} m'(0) + \frac{\xi^2}{2\tau} m''(0) + \cdots \right) \tag{27}$$

If we retain terms up to quadratic order in $\xi$, we find that the maximum of $\mathcal{R}(\xi, \tau)$ behaves as a function of time as

$$\xi_f \sim \varepsilon K \tau^{3/2} \tag{28}$$

where $K$ is a constant readily calculated in terms of $m(\rho)$ from Eq. (27). This behavior replaces the proportionality indicated in Eq. (24). Hence, there can be as many as three distinct regimes for the behavior of $\xi_f$ when $\mathcal{D} = 1$. At the very shortest times $\xi_f$ is approximately equal to a constant then it is approximately proportional to $\tau^{3/2}$, and at much longer times it approaches proportionality to $\tau^{1/2}$. The early-time crossover for $\mathcal{D} = 1$ can be seen in simulated data, as will be shown later.

We next consider the time dependence of the width of the reaction zone $w(\tau)$, which is defined in terms of $\xi_f$ by

$$w^2(\tau) = \frac{\int_{-\infty}^{\infty} (\xi - \xi_f)^2 \, R(\xi, \tau) \, d\xi}{\int_{-\infty}^{\infty} R(\xi, \tau) \, d\xi} \tag{29}$$

This width is, in the lowest order of approximation, found to be proportional to $\sqrt{\tau}$. The local production rate at $\xi_f$, which we define to be proportional to $\alpha(\xi_f, \tau) \beta(\xi_f, \tau)$, is, to the same order found to be approximately equal to a constant. These results may be contrasted with those of Gálfi and Rácz, which are valid at long times, and which predict that the width of the reaction zone will grow, at long times, as $\tau^{1/6}$, and that the maximum production rate at the center of the reaction zone decreases with time as $\tau^{-2/3}$. The physical origin of these results is readily understood through the consideration that at the very earliest times, when the reactants have only had time to mix in a very narrow region, the rate of production of C will be correspondingly small, and the main observed results are those due to diffusion rather than reaction.

Finally, we consider the width of the depletion zone, which is, roughly speaking, the zone in which substantial reaction has taken place. To characterize this zone, we use a dimensionless distance $\Delta \xi_{1/2}$, defined as the distance between the points at which the concentration profiles of A and B fall to half of their initial values. The half-height of the concentration of A is found at value of $\xi$ that is the solution to $\alpha(\xi, \tau) = 1/2$. To lowest orders in our perturbation scheme, we need to solve the equation

$$\alpha_0(\xi, \tau) + \varepsilon \alpha_1(\xi, \tau) = \Phi\left(\frac{\rho}{(2\mathcal{D})^{1/2}}\right) - \varepsilon \tau g(\rho) = \frac{1}{2} \tag{30}$$

where $g(\rho)$ is the function defined in Eq. (18). A similar equation is valid for $\beta(\xi, \tau)$. If we neglect the term proportional to $\varepsilon$, we find that the solution to Eq. (30) is $\xi = 0$; hence we expand the equation around this value, finding that $\xi_{1/2}(A)$ is proportional to $\tau^{3/2}$ at sufficiently early times. Thus, for this measure of depletion, we can also have as many as three distinguishable regimes in time. The point $\xi_{1/2}(B)$ has the same behavior, which implies that the distance between these points will also show the same dependence on time. This is valid for $\mathscr{D} \neq 1$ as well as for $\mathscr{D} = 1$.

## 3. SOME NUMERICAL RESULTS

In order to check some of the features of both Gálfi and Rácz and our own analysis, we simulated the diffusion-reaction process, making use of a modification of the exact enumeration method, which is basically equivalent to a discretization of Eqs. (1a) and (1b) both in time and space.[19-21] Essentially the same technique was used to generate results for a related problem by Muzzio and Ottino.[22-24]

Let us consider one formulation of the changes required in the exact enumeration method to deal with our present problem of a reaction between two species of particles. For this purpose we need to keep track of two sets of registers, rather than a single set, and we further split the process into a part reflecting diffusion and a part reflecting the reaction kinetics. The first part of the simulation consists of a stage simulating diffusion without reaction. Since the simulation is done on a lattice rather than a continuum as in Eqs. (1a) and (1b), we require the analog of two types of parameters, the first consisting of the pair of diffusion constants, and the second being the reaction constant $k$. Since the simulation is carried out in discrete time, this set of parameters is replaced, in our simulation technique, by a set of probabilities. For example, the diffusion constant along the $x$-direction is simulated, in the exact enumeration method, by permitting a random walker to make one of three choices on a given step. At any step of the process it is allowed to make a step to the right, to the left, or to make no step. Thus, for a symmetric random walk, we have a probability equal to $\delta$ of moving to the right or to the left, and $\eta$ of remaining in place, with $2\delta + \eta = 1$. In this picture the analog of the diffusion constant can be identified with the probability $2\delta$. This parameter can take on different values for each of the reactants. Finally, the reaction constant $k$ that appears in Eqs. (1a) and (1b) is also replaced by a probability which we denote by $\theta_n$ in the $n$th step of the simulation. The actual form of this probability will be discussed after our description of the diffusive part of the calculation.

Let us focus on the changes required at a single lattice site, call it $j$, during a single step of the simulation. There are two registers, one associated with A's and the second with B's. Let the contents of the A register corresponding to site $j$ be denoted by $a_n(j)$ and that of the B register be denoted by $b_n(j)$. The recursive step used in our implementation of the recursion will be written in terms of quantities

$$\Gamma_n(j) = \eta_A a_n(j) + \delta_A [a_n(j+1) + a_n(j-1)]$$
$$\Omega_n(j) = \eta_B b_n(j) + \delta_B [b_n(j+1) + b_n(j-1)] \tag{31}$$

as

$$a_{n+1}(j) = \Gamma_n(j)[1 - \theta_n]$$
$$b_{n+1}(j) = \Omega_n(j)[1 - \theta_n] \tag{32}$$

and the initial conditions are $a_0(j) = a_0$ for $j \geqslant 0$, $a_0(j) = 0$ for $j < 0$; and $b_0(j) = b_0$ for $j \leqslant 0$, $b_0(j) = 0$ for $j > 0$.

The second phase of the calculation takes the reaction step into account, by emulating the dynamics embodied in Eqs. (1a) and (1b), in the absence of diffusion. In this way it is possible to convert the reaction constant into a probability. When diffusion is neglected, which is equivalent to an assumption of perfect mixing, the kinetic equations are $\dot{a} = \dot{b} = -kab$. Let the initial conditions for the solution of these equations be $a(n) = A_n$ and $b(n) = B_n$, where $n$ denotes the discrete step number. After a (continuous) time $t$, the concentrations calculated from the differential equations for the kinetics are

$$A_n - a(t) = B_n - b(t) = \frac{A_n B_n [1 - R(t)]}{A_n - B_n R(t)} \tag{33}$$

in which $R(t) = \exp[-k(A_n - B_n) t]$. When $A_n = B_n$ we can take the limit in this equation to find

$$a(t) = \frac{A_n}{1 + A_n kt} \tag{34}$$

In our calculations we used the value $t = 1$, corresponding to a single step in the discrete time domain. It follows from the results given in the last two equations that

$$\theta_n = \min \left\{ \frac{B_n [1 - R(1)]}{A_n - B_n R(1)}, 1 \right\}, \qquad A_n \neq B_n$$

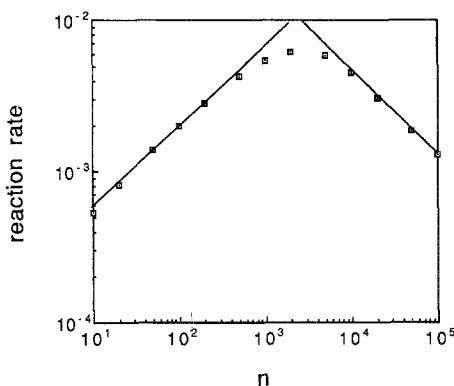$$= \frac{A_n k}{1 + A_n k}, \qquad A_n = B_n \tag{35}$$

Fig. 1. A plot of the reaction rate as a function of the number of steps $n$. These results were obtained by an exact enumeration calculation using the parameters $\delta_A = \delta_B = 1/2$, $\eta_A = \eta_B = 0$, and $k = 4 \times 10^{-4}$. Solid lines are drawn with slopes of $\pm 1/2$ for comparison. The initial slight deviation from the slope of $-1/2$ is probably the effect of discretization.

It is pertinent to mention that it is not always possible to separate diffusion from the reaction step in a simulation, as has recently been pointed out by Muzzio and Ottino.[22-24]

A number of results for our system are immediately verifiable using exact enumeration. Figure 1 shows a graph of the reaction rate as a function of step number, where the points have been obtained from an exact enumeration analysis. Our perturbation analysis predicts that the rate increases initially as $n^{1/2}$, followed by a crossover to the $n^{-1/2}$ behavior predicted by the scaling theory of Gálfi and Rácz. The two straight lines drawn in the figure have slopes equal to $+1/2$ and $-1/2$, respectively. The parameters used to generate the graph are $\eta_A = \eta_B = 0$, $\delta_A = \delta_B = 1/2$, and $k = 4 \times 10^{-4}$. Our numerical procedure was also used to check the other crossover predictions. The data plotted in Fig. 2 illustrate the crossover from the dependence $n^{1/2}$ to that of $n^{1/6}$ for the width of the front, and the crossover in the production rate at the center of the reaction zone from early time constancy to $n^{-2/3}$. Figure 3 shows the three-regime behavior predicted for $\xi_f$ when $\mathscr{D} = 1$, and Fig. 4 shows that the width of the depletion zone shares the same behavior independent of the value of $\mathscr{D}$.
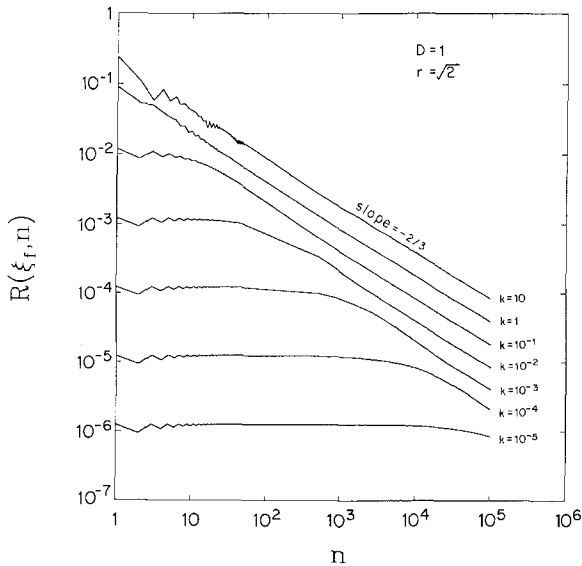
## 4. THE FRACTAL SUBSTRATE

Consider first the reaction $A + B \rightarrow C$ occurring on a homogeneous surface whose coordinates are $(x, y)$. The initial conditions will be

$$\rho_a(x, y; 0) = a_0 H(y), \qquad \rho_b(x, y; 0) = b_0 [1 - H(y)] \qquad (36)$$
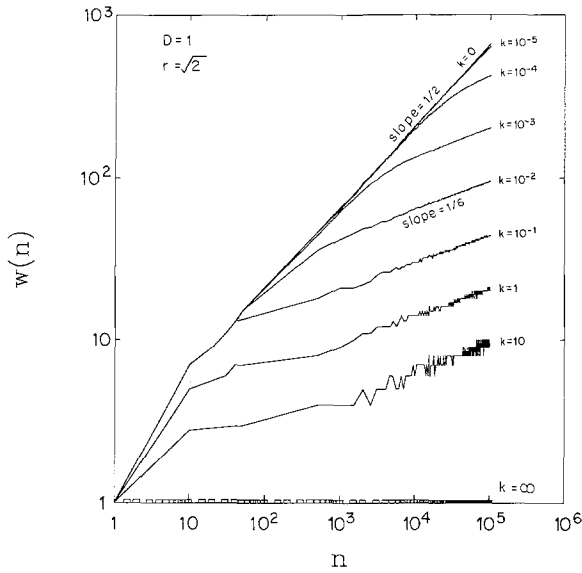
(a)



(b)

Fig. 2. Plot of the (a) width $w(n)$ and (b) local reaction rate at the center of front $R(\xi_f, n)$ as a function of the number of steps for various values of $k$ and for the parameter values $\mathscr{D} = 1$ and $r = \sqrt{2}$. In both parts of the figure we see crossover behavior as a function of $n$. The jagged edges in both graphs are artefacts of the discrete simulation.
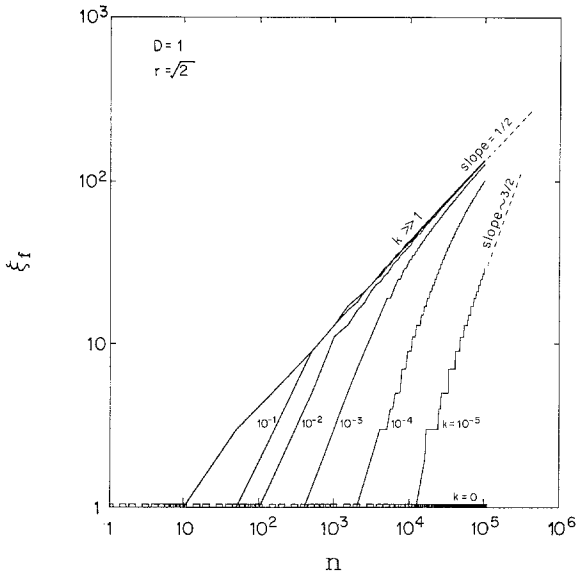
Fig. 3.  Several curves of $\xi_f$ as a function of $n$, which illustrate the three-regime behavior for $\mathscr{D} = 1$. Crossovers are seen from the very early constant to $n^{3/2}$, and from $n^{3/2}$ to the asymptotic $n^{1/2}$. The transition point clearly depends on the rate coefficient $k$.
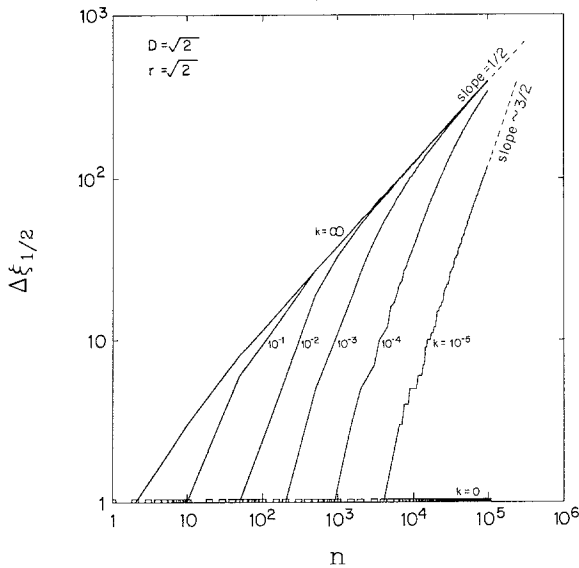


Fig. 4.  A plot of $\Delta \xi_{1/2}$ [equal to $|\xi_{1/2}(A) - \xi_{1/2}(B)|$] as a function of $n$, showing that the very earliest dependence is constant, following which there is a crossover to proportionality to $n^{3/2}$, and finally to the asymptotic $n^{1/2}$. The specific parameters used are $\mathscr{D} = \sqrt{2}$ and $r = \sqrt{2}$. Similar results are obtained for $\mathscr{D} = 1$.

so that the reactants are initially separated by the line $y = 0$. The size of the system along the $x$ coordinate is taken equal to $L$ whereas it is assumed to be infinite along the $y$ axis. When the reaction-diffusion equation is that shown in Eqs. (1a) and (1b), we expect that both the results derived for the short-time behavior in Section 2 and the scaling theory of Gálfi and Rácz will remain basically unchanged.[18] This is due to the mean-field nature of our model.

In order to observe any deviations from predictions based on the reaction-diffusion equations (1a) and (1b), we consider the reaction to occur on a fractal surface. Specifically, we will model the transport process in terms of a random walk on a percolation system rather than as a diffusion process in a homogeneous medium. The numerical analysis of the random walk to confirm our scaling predictions was also carried out in this case by the method of exact enumeration. Let $d_f$ be the fractal dimension of the medium in which the reaction-diffusion process takes place, and let $d_w$ be the diffusion exponent, defined in terms of the mean-squared displacement after $n$ steps, $\langle r^2(n) \rangle$, through the relation

$$\lim_{n \to \infty} \langle r^2(n) \rangle / n^{2/d_w} = \text{const}$$

The length of the interface, because of the irregular structure, is of the order of magnitude of $L^{d_f - 1}$.

A crude scaling argument can be used to suggest analogs to the predictions of Gálfi and Rácz. The amount of C produced in $n$ steps in time, $N_C(n)$, is approximately proportional to the length of the interface multiplied by a typical displacement, $r(n) \equiv \langle r^2(n) \rangle^{1/2}$, during that time. Hence we can write

$$N_C(n) \sim L^{d_f - 1} r(n) \sim L^{d_f - 1} n^{1/d_w} \tag{37}$$

where we have omitted some constants which play no role in our argument. Hence our argument predicts that the rate of production of C, obtained by differentiating Eq. (37), is asymptotically proportional to $n^{-(1 - 1/d_w)}$. This reduces to the correct prediction for the homogeneous medium, in which $d_w = 2$.

To check our prediction in the more general case, in addition to determining the time dependence of the height at the reaction center and the width of the reaction zone, we carried out a simulation study, using as a model of the fractal a two-dimensional percolation system approximately at criticality, i.e., the probability that a site is blocked was set equal to 0.4, so that the proportion of sites available for transport is 0.6. This is close

to the percolation threshold value $p_c \sim 0.593$. The results in our numerical investigation represent an average of data taken on 200 realizations of the percolation system. The initial conditions set a particle, A or B, on each live site, the A's in the right-hand plane, and the B's in the left-hand plane, and each particle must move at each step with equal probability to each unoccupied site. The reaction probability was taken equal to 1, so that reaction on collision is a certainty.

Figure 5 contains a log-log plot of the rate of production of C as a function of the time, the slope found from our simulated data being equal to $-0.664$, compared with the predicted value, which is known approximately[21] to be quite close to $-(1 - 1/d_w) \sim -0.65$. Because of local fluctuations in properties of the lattice, one expects to see a wider reaction zone than is the case for a random walk on a uniform lattice. In Figs. 6a and 6b we present results for the width and height of the reaction zone as a function of $n$. These results are consistent with the scaling forms

$$w(n) \sim n^{1/d_w} \tag{38a}$$

$$h(n) \sim n^{-1} \tag{38b}$$

at sufficiently large step numbers.

Both of the exponents in (38a) and (38b) differ significantly from the values predicted by Gálfi and Rácz for diffusion in a homogeneous space. The differences are undoubtedly due to spatial fluctuations in the structure of the substrate, which allows particles of a given variety to easily penetrate the part of the lattice initially occupied by a lesser number of particles of
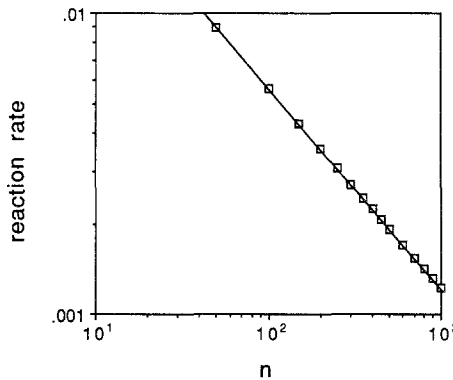


Fig. 5.   The reaction rate plotted as a function of $n$ for a two-dimensional percolation system very close to criticality. The slope is found to be approximately equal to $-0.664$, as against the expected $-0.65$.

the complementary species. This effect does not occur on a translationally invariant lattice, where the diffusion process remains homogeneous over the entire substrate. Some evidence in support of this qualitative explanation is provided by a plot of the concentration of one of the species as a function of distance from the interface at a number of times, as shown in Fig. 7. The curves shown represent data from an average of 100 runs. The somewhat surprising feature of these curves is that the concentration very close to the interface increases rather than decreases with increasing time. This does not occur in a homogeneous system in which reaction is instantaneous. The difference between these two cases is due to the fact that in the former case one of the species of reactant particles can migrate into the region without finding a corresponding member of the second species
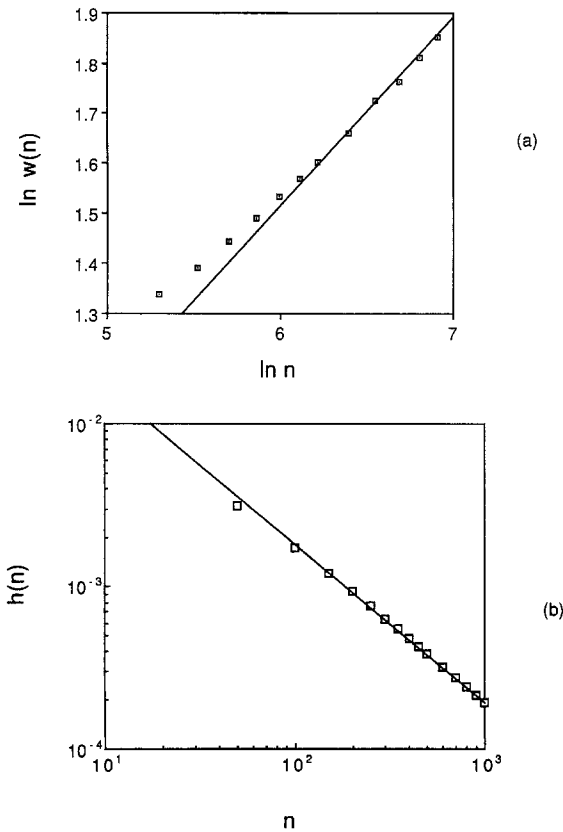


Fig. 6. Data for (a) the width $w(n)$ and (b) the height $h(n)$ as a function of step number. The indicated slopes are 0.375 for the width and $-0.99$ for the height, which are very close to the values given in (38a) and (38b).
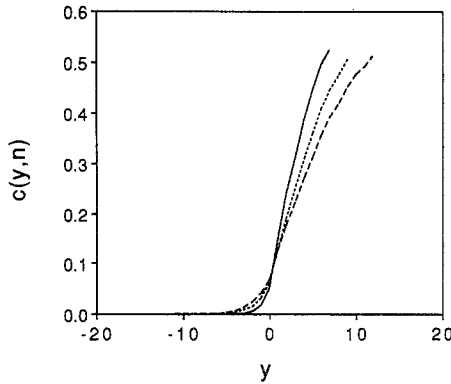
Fig. 7. Plots of the concentration profile for one of the species shown as a function of $y$, for $n = 100$ (—), 300 ($\cdots$), and 600 (– –) for a percolation substrate in two dimensions that is close to criticality. The interesting feature in this figure is the increase in $c(y, n)$ for $y < 0$.

with which to react. In Fig. 8 we replot the concentration profile $c(y, n)$ at different times as a function of the scaling parameter

$$\zeta = y(n)/y_0(n) \tag{39}$$

where, for large $n$, the offset parameter $y_0(n)$ is proportional to $n^{1/d_w}$. Such a scaling form appears to be validated by our data. The linear slope found in the semilog plot in Fig. 8 at small values of $\zeta$ suggests that in this range

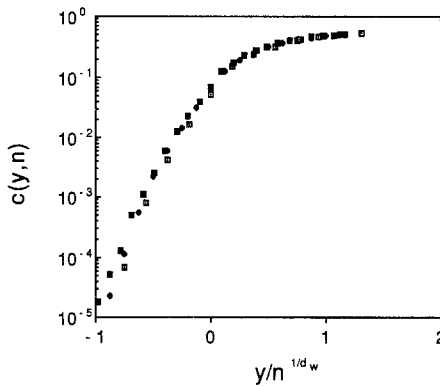$$\ln c(y, n) \equiv \ln c(\zeta) \sim U - V\zeta \tag{40}$$



Fig. 8. A semilog plot of data for the concentration profile of one of the species as a function of the similarity parameter $\zeta = y/n^{1/d_w}$ with the indicated scaling behavior at lower values of this parameter.

where $U$ and $V$ are constants. A heuristic argument can be advanced to support this form of the concentration profile. When reaction is instantaneous in a uniform continuum there can be no particles at the point $y = 0$. This property does not necessarily hold in the case of an irregular or fractal substrate, which suggests that $c(y, n)$ can be expanded to lowest order in $\zeta$ as

$$c(y, n) \sim c_0 + c_1 \zeta, \qquad c_0 \neq 0 \tag{41}$$

which agrees with the first term in the expansion of Eq. (40) in a power series in $\zeta$. If one combines Eq. (40) with the two scaling assumptions of Gálfi and Rácz, one easily finds the exponents for the width and height of the reaction zone given in (38a) and (38b).

Finally, we mention that we have studied another quantity relevant for one-dimensional systems in which the reaction between two particles that meet is certain. This is the average of the closest distance separating an A–B pair after a time $t$. This can be regarded as a much simplified model for the self-segregation effect operative in low-dimensional systems. It has been shown[25-27] that when there is a single B which is a trap (i.e., the reaction is $A + B \rightarrow B$) the expected distance between the B and the closest untrapped A scales as $t^{1/4}$ at sufficiently long times. Our Monte Carlo simulations indicate that for the $A + B \rightarrow C$ reaction the scaling behavior of the nearest-neighbor distance also scales as $t^{1/4}$ for all sets of diffusion constants. This work will be presented elsewhere.

## ACKNOWLEDGMENTS

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