BRIEF REPORTS

Experimental study of a ternary $A+2B\rightarrow C$ reaction-diffusion system with a propagating reaction front: Scaling exponents

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We study experimentally the $A+2B\rightarrow C$ reaction-diffusion process with initially separated reagents in a capillary using an inorganic chemical reaction. We measure and compare with theory the dynamic quantities that characterize the kinetic behavior of the system: the global reaction rate $R(t)$, the location of the reaction center $x_f(t)$, the front's width $w(t)$, and the local production rate $R(x_f,t)$. We demonstrate the nonclassical phenomena of reactant segregation and depletion-zone formation for this reaction-diffusion process. The experimental results are in good agreement with theory and simulation and quite different from the exponents for the elementary binary $A+B\rightarrow C$ reaction. The time exponents are 0.27 for the width, -0.48 for the global reaction rate, and -0.75 for the local reaction rate, compared to theoretical values of 0.25, -0.5, and -0.75, respectively. [S1063-651X(97)01509-2]

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We report here an experimental study of a ternary reaction-diffusion system with a propagating front. Previous such studies were limited to binary elementary reactions. These fronts play an important role in many problems. The presence of such a reaction interface is characteristic of many processes in nature [1–5].

The pioneering work along this line is due to Galfi and Racz [6]. They considered the kinetics at long times of an effectively one-dimensional reaction-diffusion system for $A+B\rightarrow$products in which A and B species are initially separated [6]. In this geometry, reactants A of constant concentration a_0 and B of constant concentration b_0 are initially separated [6]. They meet at time 0, forming a reaction front. The following set of reaction-diffusion equations for the local concentrations a,b is assumed to describe the system:

$$\frac{\partial a}{\partial t}=D_a\nabla^2 a-kab, \quad \frac{\partial b}{\partial t}=D_b\nabla^2 b-kab, \quad (1)$$

where k is the microscopic local reaction constant. The equation must satisfy the initial separation condition along the separation axis x,

$$a=a_0 H(x), \quad b=b_0[1-H(x)], \quad (2)$$

where $H(x)$ is the Heaviside step function. Galfi and Racz showed that for the elementary $A+B\rightarrow C$ reaction in the long-time limit the center of the reaction front (x_f) and the width (w) of the front scale with time as $x_f\sim t^{1/2}$ and $w\sim t^{1/6}$, respectively, while the production rate of C at x_f, $R(x_f,t)$, is proportional to $t^{-2/3}$.

This binary reaction front system has been implemented experimentally [7,8] by the reaction

$$Cu^{2+}+(tetra)\leftrightarrow 1:1 \text{ complex.} \quad (3)$$
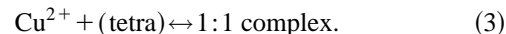
Experimental results agreed well with theoretical and numerical predictions [7–9] $w\sim t^{0.17}$, $x_f\sim t^{0.51}$, and $R(x_f,t)\sim t^{-0.51}$. This work has been of much recent interest [10–12].

The generalized and more complicated $nA+mB\rightarrow C$ reactions under an initially separated condition were also studied theoretically. Cornell, Droz, and Chopard predicted exponents for the generalized $nA+mB\rightarrow C$ reactions based on the mean-field approximation. They found the width to scale as $t^{n+m-1/2(n+m+1)}$ and the production rate of C at x_f, $R(x_f,t)$, to scale as $t^{-(n+m)/(n+m+1)}$ [13,14]. The global rate $R(t)$, which is defined by the integral of the local rate over space, is always proportional to $t^{-1/2}$ independent of n,m. Later Cornell, Koza, and Droz [15] used a multiscaling analysis and numerical simulation to confirm the finding for dimensions $d>d_c\equiv 2/(m+n-1)$. Here we present an experimental realization for a ternary $A+2B\rightarrow C$ reaction and find good agreement between theory and experiment in a convectionless capillary solution. Our Monte Carlo simulation results also agree with the theory.

In order to monitor the dynamical quantities of the reaction front at the asymptotic time limit we needed a reaction that meets the following requirements: (i) fast enough to ensure the diffusion-limited condition, (ii) a one-to-two termolecular reaction, and (iii) the existence of a suitable detection
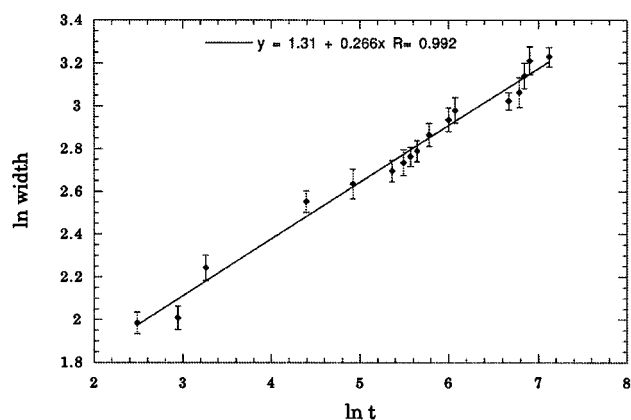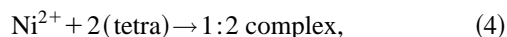
FIG. 1. ln$w$ vs ln$t$. The exponent in the asymptotic regime is 0.27. The unit for the width is 0.1 mm.

method for the reactant(s) and product. Therefore, in contrast to the copper-ion reaction [3], we chose to use the nickel-ion reaction

$$Ni^{2+} + 2(tetra) \rightarrow 1:2 \text{ complex},\qquad(4)$$

where "tetra" is disodium ethyl bis(5-tetrazolylazo)acetate trihydrate [16]. This is a fast 1:2 complex formation reaction, so we expect the system to follow an asymptotic behavior at a relatively early time. We can also easily monitor the properties of the front by monitoring the absorbance of the product.

As reactants $3.38 \times 10^{-5} M$ of tetra and $1.06 \times 10^{-3} M$ of Ni^{2+} were used, with a 0.35% water solution of gelatin. The addition of gelatin increases the viscosity, preventing convection and ensuring the formation of a sharp boundary at time zero [7,8]. The apparatus and methods were similar to those reported before [7,8]. The absorbance profiles of the product formation along the length of the reaction vessel are obtained by scanning along a defined length of the reactor, in parallel with the detector, using the system described in detail [7,8]. The absorption wavelength for the inorganic nickel product excitation is 500 nm and for the reactant tetra excitation it is 400 nm. We used a halogen lamp and two bandpass filters: 500 ± 10 nm for the product and 400 ± 8 nm for the reactant, tetra.
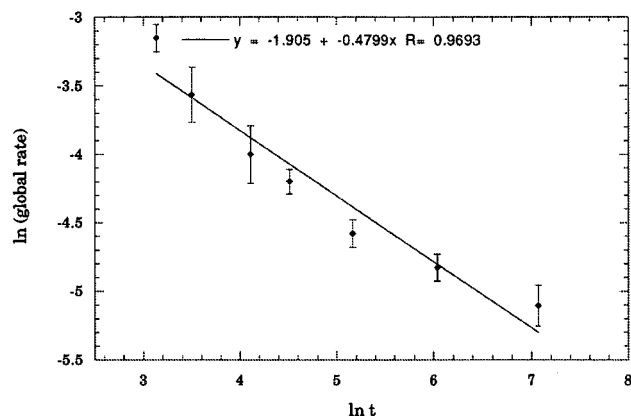

FIG. 2. ln(global rate) vs ln$t$. The unit for the global rate is absorbance/min. The exponent in the asymptotic regime is -0.48. Compare with the simulation (Fig. 4).
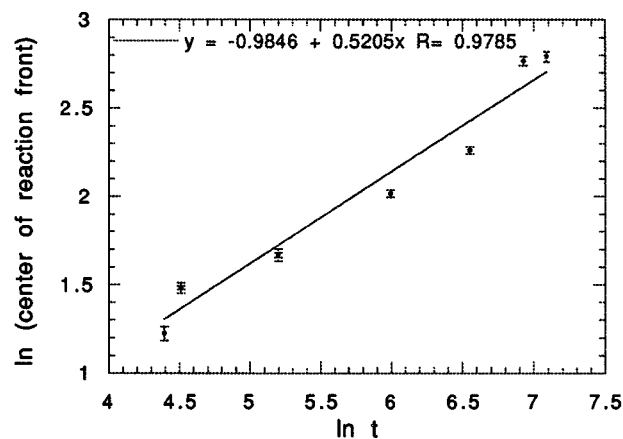

FIG. 3. ln(center of the reaction front) vs ln$t$. The exponent in the asymptotic regime is 0.52. The unit for the center of the front is mm.

The absorption maxima of the reactant, tetra, and the product are well separated and the absorbance of nickel ions is negligible. Both the reactant tetra and the product obey the Beer-Lambert law under experimental conditions. The optical absorbance of the total accumulated product is measured along the reaction front domain at fixed time intervals. From the difference in absorbance of the total product measured at consecutive times we find the product formation per unit time at each moment and determine the time exponents for the dynamical properties. The center of the reaction front is defined as the position with the highest product formation rate for any given time t. Experimentally, it is defined as the position with the highest product absorbance. The reaction front width is determined from the half-width of each subtraction profile. We define the global rate as the integral of the local rate $R(x_f,t)$ over the whole space. The rate is determined by the change of the product formation per unit time. To determine the critical exponents for the dynamic exponents we fit the log-log plots (Figs. 1–3). The experimental results and the theoretical expectations are shown in Table I. The local reaction rate is somewhat difficult to monitor experimentally. We calculated its exponent from the relationship of the exponent for the width and the global reaction rate. From scaling arguments the exponent of the local rate equals the exponent of the global rate minus the exponent of the width [7]. We see excellent agreement between the long-time experimental results and asymptotic theoretical predictions, as well as with the simulation results (see below).

TABLE I. Comparison of time exponents.

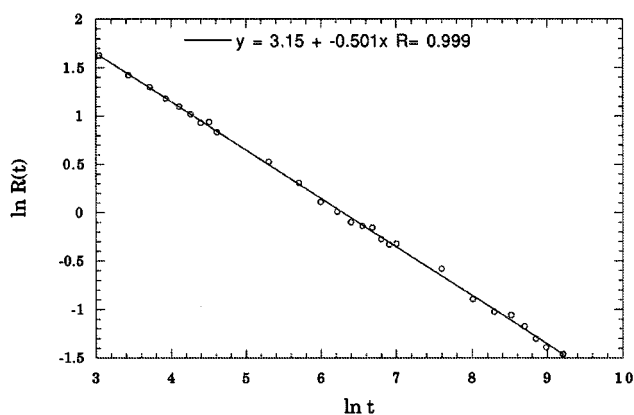| Method	Width	Center of front	Global rate	Local reaction rate
Experiment	0.27 ± 0.05	0.52 ± 0.05	-0.48 ± 0.05	-0.75 ± 0.1
Theory	0.25	0.50	-0.50	-0.75
Simulation			-0.50	
Classical	0.5	0	$+0.5$	0

FIG. 4. Simulation result for ln(global rate) vs ln$t$. The exponent is -0.50. Compare with the experiment (Fig. 2).

Figure 4 shows the global rate versus time data on a log-log scale simulated on the square lattice (200×200) under initial reactant separation using the Monte Carlo method. Particle probabilities of 40% for A and 80% for B are placed at opposite sides of the origin at time 0. The diffusion coefficients are the same for A and B. When A and B meet an intermediate (AB) is formed. Then, if the intermediate meets with a B particle they will react and leave the system. The result is averaged over 1000 runs. The global reaction rate exponent is -0.50, which agrees with theory and experiment.

In conclusion, we have studied experimentally a termolecular $A+2B\rightarrow C$ reaction-diffusion process with initially separated components. We find that the $Ni^{2+}+2(tetra)\rightarrow1{:}2$ complex formation reaction indeed shows the segregation of the reactants and gap formation. The global rate exponent goes as $t^{-1/2}$, the same as for the simple $A+B\rightarrow C$ reaction under initial segregation. The critical exponents are in good agreement with the theory for the generalized $nA+mB\rightarrow C$ system and with the simulations.

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