

Experimental study of a crossover from nonclassical to classical chemical kinetics: An elementary and reversible $A + B \leftrightarrow C$ reaction-diffusion process in a capillary

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We study an elementary and reversible $A + B \leftrightarrow C$ reaction-diffusion process with initially separated reagents, in a convectionless capillary, using an inorganic chemical reaction. We show that the dynamics of the system can be described in terms of a crossover between an “irreversible regime” and a “reversible regime.” We measured the critical exponents in both regimes. In the irreversible regime we demonstrate the nonclassical phenomena of reactant segregation and depletion-zone formation. In the reversible regime we observed the effect of a local equilibrium where the classical prediction is confirmed. The experimental results are in good agreement with values predicted by theory and simulation. [S1063-651X(96)04109-8]

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I. INTRODUCTION

There has been a resurgence of interest in diffusion-controlled reaction kinetics [1–21]. Theoretically, a better understanding has been achieved regarding the way spatial dimensionality affects diffusion, fluctuations, and stochastic processes in general. Computer and supercomputer simulations have demonstrated, verified, and expanded many of these theories. Experimentally there has also been work on the reactions of the forms $A + A \rightarrow$ products [6–8] and $A + C \rightarrow C +$ products [9,10]. However, there has been little progress regarding the most important class of reactions, $A + B \rightarrow$ products. This is not only the most common and important class of reactions, but also the one where the most drastic deviations from classical behavior have been predicted theoretically and demonstrated in computer simulations [1–5,10–21].

Galfi and Racz 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 [11]. In this geometry, reactants A of constant concentration a_0 and B of constant concentration b_0 are initially separated. They meet at time 0, forming a reaction front. The presence of a reaction front is a characteristic feature of a variety of physical, chemical, and biological processes [12–20]. Galfi and Racz assumed the following set of reaction-diffusion equations for the local concentrations a, b to describe the system:

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

$$\frac{\partial b}{\partial t} = D_b \nabla^2 b - kab,$$

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 in the long-time limit the center of the reaction front (x_f) and the width of the front (w) 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 system has been implemented experimentally [13]. The experimental results agree well with theoretical predictions, $x_f \sim t^{0.51}$, $w \sim t^{0.17}$, and $R(x_f, t) \sim t^{0.70}$. Simulation [14,15] results also show good agreement with theoretical prediction, $x_f \sim t^{0.52}$, $w \sim t^{0.16}$, and $R(x_f, t) \sim t^{0.68}$.

In reality, most, if not all, chemical reactions are reversible, given enough time. It was shown by Chopard, Droz, Karapiperis, and Racz [21] that the reversible $A + B \leftrightarrow C$ reaction-diffusion process with initially separated components can be described in terms of a crossover between an “irreversible” regime at short times and a “reversible” regime at long times. In the “irreversible” regime the exponents agree with those predicted by Galfi and Racz [11]. In the “reversible” regime, because of the existence of a local equilibrium at the reaction front, the dynamics is governed only by the diffusion process and the critical exponents are correctly given by the mean-field approximation $w \sim t^{1/2}$, $R(x_f, t) \sim \text{const.}$, independent of the dimension. The crossover time τ is inversely proportional to the backward reaction constant [21].

Here we present an experimental realization of a reversible elementary reaction and find good agreement between theory and experiment in a convectionless capillary solution.

II. EXPERIMENT

A. Reaction

In order to monitor the dynamical quantities of the reaction front we need a reaction that meets the following requirements: (i) it must be fast enough to ensure the diffusion-limited condition; (ii) it must have a one-to-one elementary

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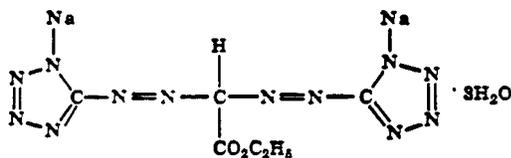


FIG. 1. Structure of "tetra."

bimolecular reaction; and (iii) there must be the existence of a suitable detection method for the reactant(s) and product. Unfortunately, only a few reactions meet the ideal criteria. We chose to use the reaction



where "tetra" is disodium ethyl bis(5-tetrazolylazo) acetate trihydrate. As reactants, $5.03 \times 10^{-5} M$ of tetra and $1.04 \times 10^{-3} M$ of Cu^{2+} were used, with a 0.65% water solution of gelatin. The addition of gelatin increases the viscosity, preventing convection and assuring the formation of a sharp boundary at time zero.

B. Materials

We synthesized disodium ethyl bis(5-tetrazolylazo) acetate trihydrate (abbreviated "tetra" in this paper) (Fig. 1) [22] as follows: 28.4 ml of 20% of sodium nitrite is added to a cooled solution of 5-aminotetrazole monohydrate in 40 ml of 20% of sodium hydroxide. 60 g of ice is added to the solution and the slurry was poured with vigorous stirring into 28.4 ml of concentrated hydrochloric acid, 120 ml of water, and 200 g of crushed ice. After 20 min, 50 g of sodium acetate trihydrate in 100 ml of water is added, followed by 13 ml of ethyl acetoacetate. The solution immediately develops an intense red color. The mixture is stirred for 2 h in an ice water bath. 100 g of sodium chloride is added near the end of the stirring period. The resulting solution is placed in a refrigerator at 5 °C for a week. During this time the product slowly crystallizes. The orange-red solid product is separated by suction filtration and is air dried.

Elementary analysis of the sample shows results well matched with the calculated results (Table I). The absorption maxima for "tetra" also matches well with the literature values of 270 and 410 nm [22].

C. Reactor

To get rid of the effect of gravity, we use a horizontal reactor (Fig. 2), different from the vertical reactors used to measure diffusion coefficients in the 1930s and 1940s [23]. The glass reactor is a rectangular tube (4×2 mm inside diameter). A central hole, drilled by a special drill so as not to change the inside surface of the reactor, is used as an air outlet.

TABLE I. Elemental analysis of "tetra."

	Calculated	C, 19.05%	H, 3.20%	N, 44.44%	Na, 12.16%
Found	C, 19.23%	H, 2.90%	N, 42.72%	Na, 11.95%	

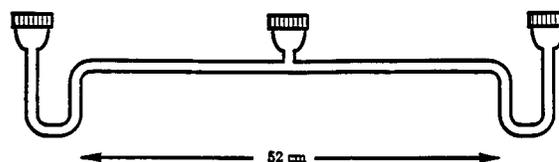


FIG. 2. Glass reactor.

D. Apparatus

Optical absorbance measurements are used to monitor the dynamic quantities of the reaction. 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 (Fig. 3). The system consists of a halogen lamp, a solenoid with two optical filters, a slit unit, and a stepping motor. We use a photomultiplier tube (PMT) in a PMT housing as the detector. The digitized output of the PMT through the A/D board contains noise. For noise reduction, we add an electronic low-pass filter and average the signal at each data point. The slit unit is composed of two slits, which are well aligned. Each slit is of size 4×1.8 mm with two movable matching stainless steel blades that cover the hole. We use a slit width of 0.05 mm on the light source side and 0.09 mm on the detector side to ensure a 0.1 mm mechanical resolution. The absorption wavelength for the inorganic product excitation is 570 nm and for the reactant "tetra" excitation it is 400 nm (Fig. 4). We use a halogen lamp and two band-pass filters, 570 ± 10 nm for the product and 400 ± 8 nm for the reactant, tetra. The on-off of the lamp and solenoid are controlled through the parallel port of the computer and the movement of the stepping motor is controlled via a stepping motor controller. The light source, solenoid with two filters, slit unit, and detector are fixed on the stepping motor and the glass reactor is fixed over the slit unit, separated from all other units. The PMT is

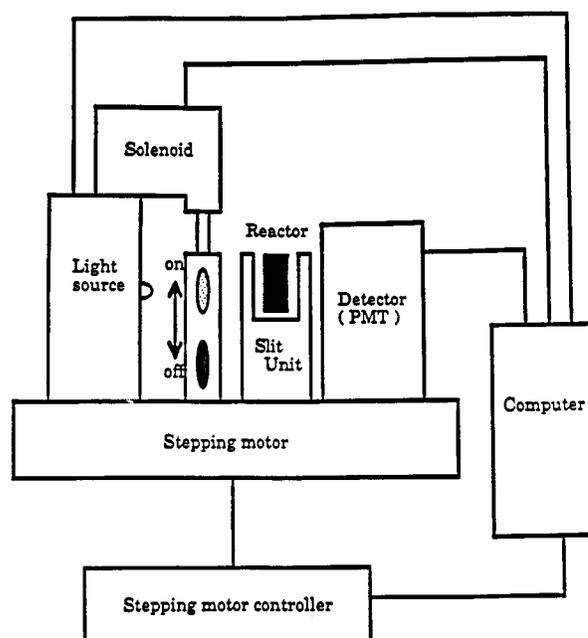


FIG. 3. Schematic diagram for the experimental setup for the optical absorbance measurement along the reaction front domain.

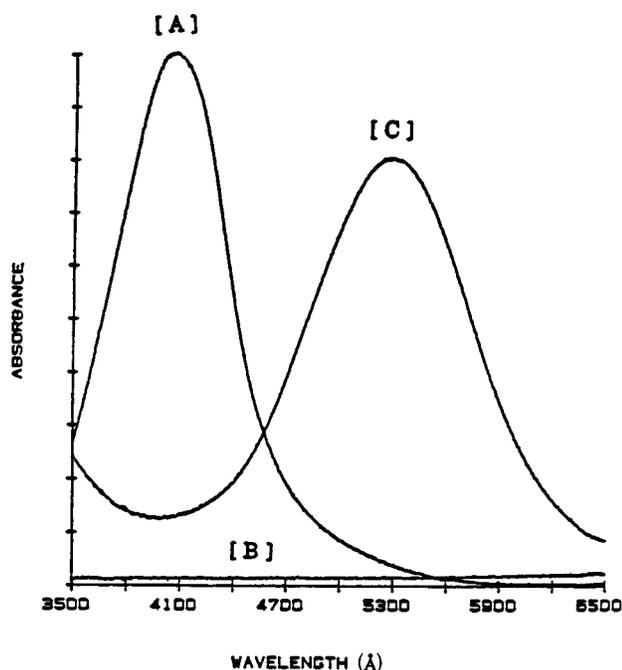


FIG. 4. The absorption spectra of "tetra" (A), Cu^{2+} (B), and the product (C). The initial concentration of the copper ion is $2 \times 10^{-3} M$, those for the "tetra" and the product were $6 \times 10^{-5} M$. Absorbance is in arbitrary units.

connected to the A/D board of the computer to convert the analog data into digital data, which is then stored by a computer.

E. Procedure

The two reactants are injected into the two end arms of the reactor using a syringe. They meet at the center of the reactor at time 0, forming a vertical boundary. The first scan along the reaction front starts when the reactants meet. The time interval between scans increases from the order of 1 min to the order of 100 min. The lamp is turned "on" 4 min before each scan. A solenoid switches back and forth between product and reactant filters. When the solenoid is on, the top filter is used, and when off, the bottom filter is used.

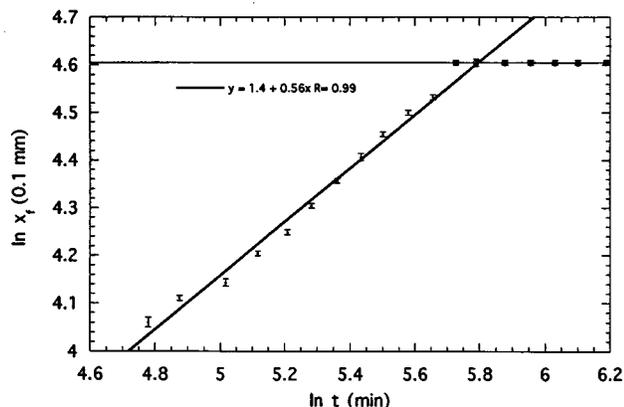


FIG. 5. $\ln x_f$ vs $\ln t$. The critical exponent in the "irreversible regime" is 0.56 and in the "reversible regime" it is 0.

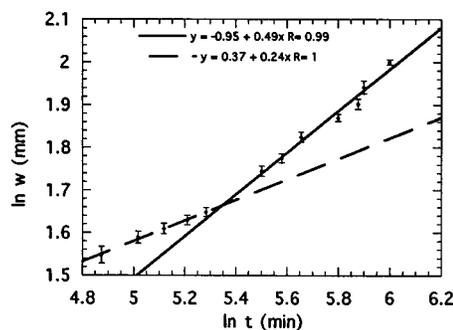


FIG. 6. $\ln w$ vs $\ln t$. The exponent crosses over from 0.24 in the "irreversible regime" to 0.49 in the "reversible regime."

The scanning process consists of the following steps: (i) the stepping motor moves, corresponding to the experimental resolution of 0.1 mm; (ii) 31 data are taken at each point and sent to the A/D board and averaged; (iii) repeat (i) and (ii) until the motor reaches the end of the reaction domain. After each scan the data are stored and the stepping motor is returned to its original position and stays there until the next scan. Each scan takes 3 s to complete. A typical run lasts about 8 h and consists of around 50 scans along the reaction front.

III. RESULTS AND DISCUSSION

The absorption maxima of the product and the reactant "tetra" are well separated and the absorbance of copper is negligible (Fig. 4). Both the product and the reactant "tetra" 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 of 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 subtracted product absorbance. The reaction front width is determined from the half width of each subtraction profile. We define the global rate $R(t)$ as the integral of the local reaction rate $R(x_f, t)$ over the x coordinate. The global rate is determined experi-

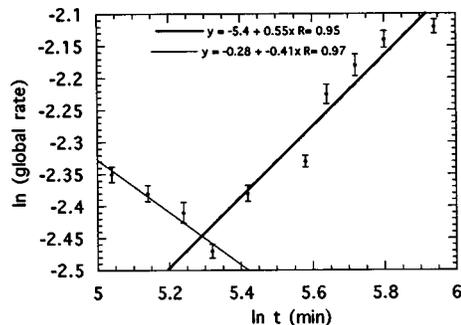


FIG. 7. \ln (global rate) vs $\ln t$. The unit for global rate is in (absorbance/min). The exponent crosses over from -0.41 in the "irreversible regime" to $+0.55$ in the "reversible regime."

TABLE II. Comparison of time exponents.

	Width		Center of the front		Global rate	
	Early	Late	Early	Late	Early	Late
Experiment	0.24 ± 0.05	0.49 ± 0.04	0.56 ± 0.05	0 ± 0.03	-0.41 ± 0.06	0.55 ± 0.05
Theory	0.17	0.50	0.50	0	-0.50	0.50

mentally as the change of the total product formation per unit time.

From the log-log plots (Figs. 5–7) we see a clear crossover for each of the three critical exponents. To determine the critical exponents in both the “reversible” and the “irreversible” regimes, we fit the log-log plots before the crossover, as well as after the crossover. The experimental results and the theoretical expectations are shown in Table II. For all our runs the crossover occurred at a time around 250 min. Thus the reverse reaction rate constant is roughly $4 \times 10^{-3} \text{ min}^{-1} M^{-1}$.

In the “irreversible regime” the experimental exponents are in good agreement with the nonclassical theoretical values predicted by Galfi and Racz. At long times, there is a formation of a local equilibrium at the reaction front, because the reversible reaction becomes a sufficiently self-mixing process and the critical exponents are correctly given by the mean field approximation. This experiment shows the existence and persistence of the reaction segregation effects for a simple elementary bimolecular reaction at early time

(irreversible regime) and then, due to the reversibility of the reaction, the system moves into a “reversible” regime where the system is described correctly by mean field theory, the classical approach.

In conclusion, we have studied experimentally an elementary, reversible $A + B \leftrightarrow C$ reaction-diffusion process with initially separated components. We find that the Cu^{2+} + “tetra” \leftrightarrow 1:1 complex formation reaction indeed shows a crossover in the reaction dynamics, from the early irreversible time regime to the late reversible time regime. The critical exponents, as expected theoretically, also show this crossover, and this crossover also gives the reverse rate constant.

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- [1] A. A. Ovchinnikov and Ya. B. Zeldovich, *Chem. Phys.* **28**, 215 (1978).
 - [2] D. Toussaint and F. Wilczek, *J. Chem. Phys.* **78**, 2642 (1983).
 - [3] K. Kang and S. Redner, *Phys. Rev. Lett.* **52**, 955 (1984).
 - [4] K. Linderberg, B. J. West, and R. Kopelman, *Phys. Rev. Lett.* **60**, 1777 (1988).
 - [5] R. Kopelman, *Science* **241**, 1620 (1988).
 - [6] R. Kopelman, S. J. Parus, and J. Prasad, *Chem. Phys.* **128**, 209 (1988).
 - [7] P. Argyrakos and R. Kopelman, *Phys. Rev. A* **41**, 2114 (1990).
 - [8] C. R. Doering and D. Ben-Avraham, *Phys. Rev. A* **38**, 3035 (1988).
 - [9] G. Weiss, R. Kopelman, and S. Havlin, *Phys. Rev. A* **39**, 466 (1989).
 - [10] H. Taitelbaum, R. Kopelman, G. H. Weiss, and S. Havlin, *Phys. Rev. A* **41**, 3116 (1990).
 - [11] L. Galfi and Z. Racz, *Phys. Rev. A* **38**, 3151 (1988).
 - [12] H. Taitelbaum, S. Havlin, J. E. Kiefer, B. Trus, and G. H. Weiss, *J. Stat. Phys.* **65**, 873 (1991).
 - [13] Y.-E. L. Koo and R. Kopelman, *J. Stat. Phys.* **65**, 893 (1991).
 - [14] Y.-E. L. Koo, L. Li, and R. Kopelman, *Mol. Cryst. Liq. Cryst.* **183**, 187 (1990).
 - [15] Z. Jiang and C. Ebner, *Phys. Rev. A* **42**, 748 (1990).
 - [16] S. Cornell, M. Droz, and B. Chopard, *Phys. Rev. A* **44**, 4826 (1991).
 - [17] B. Chopard and M. Droz, *Europhys. Lett.* **15**, 459 (1991).
 - [18] M. Araujo, S. Havlin, H. Larralde, and H. E. Stanley, *Phys. Rev. Lett.* **68**, 1791 (1992).
 - [19] H. Larralde, M. Araujo, S. Havlin, and H. E. Stanley, *Phys. Rev. A* **46**, 855 (1992).
 - [20] H. Larralde, M. Araujo, S. Havlin, and H. E. Stanley, *Phys. Rev. A* **46**, R6121 (1992).
 - [21] B. Chopard, M. Droz, T. Karapiperis, and Z. Racz, *Phys. Rev. E* **47**, R 40 (1993).
 - [22] H. Jonassen, V. Chamblin, V. Wagner, Jr., and R. Henry, *Anal. Chem.* **30**, 1660 (1958).
 - [23] H. Neurath, *Science* **93**, 431 (1941).