Enhancement of the reactivity by chaotic mixing

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We report an experimental study of chaotic mixing of chemically reacting species, for first- and second-order reactions, in a system composed of a pair of like-sign vortices, oscillating periodically in time. For the second-order reaction, we find that the overall reactivity is enhanced compared to homogeneous mixing. This provides experimental evidence that chaotic mixing may increase the overall reaction rate for second-order reactions. We offer a method to estimate the global reactivity, which underlines the role of the concentration filaments formed, in the system, by the chaotic process. [S1063-651X(97)15108-X]

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I. INTRODUCTION

Mixing of chemically reacting species is a wide subject which has been tackled for many years by chemical engineers. The discovery of chaos and its implications on mixing processes have stimulated new approaches. Several phenomena have been studied numerically in systems where chaotic mixing takes place. Some provide a chemical signature of the divergence of trajectories in the phase space: This is the case when two similar competitive reactions are chaotically mixed [1]. Here we consider another phenomenon, which has been sort of foreseen some time ago [2], but, to the best of our knowledge, has never received a full experimental investigation: This effect is expected when a chemical reaction with a nonlinear kinetics takes place in a chaotically mixed system. In this situation, one anticipates that the reaction proceeds rapidly in high-concentration regions and slowly in low-concentration regions, so that eventually (because of the nonlinear kinetics) one gets a global enhancement of the reaction rate, in comparison with pure homogeneous mixing. This phenomenon probably plays a role in the context of ozone destruction in the polar stratosphere, as recently proposed [3–6]. The purpose of this paper is to present an experimental investigation of this effect.

II. EXPERIMENTAL SETUP

The experimental system is represented in Fig. 1: The flow develops in a thin layer of fluid, 2 mm in thickness, contained in a cell of dimensions 11×8 cm^2. The fluid is a conducting solution whose nature depends on the chemical reaction we consider; it will be further described. The flow is driven by electromagnetic forces, due to the interaction of a uniform, horizontal electrical current, and a magnetic field produced by permanent magnets, located just below the fluid [7]. For these experiments, the magnets are arranged so that the flow structure is a pair of corotating vortices, rotating in the plane of the fluid layer (see Fig. 1). We use an alternating current, of intensity $I = 120$ mA and frequency $f = 125$ mHz. The hyperbolic point located between the two like-sign vortices oscillates in space, which is precisely the required conditions to get chaotic mixing [8,9].

Concerning the chemical reaction, we consider here two distinct cases, corresponding to first- and second-order kinetics which are, respectively, linear and nonlinear in the con-

centration; this is done in order to show that in this problem the kinetics of the reaction plays a crucial role. In all cases, the solution where the flow develops is composed of a mixture of a solvent, one of the reactants, and a specific indicator. According to the protocol we use, the second reactant is injected close to the hyperbolic point of the flow, after the current has been switched on; the concentration of product is given by that of the indicator. We follow the temporal evolution of the concentration field of product by using a video camera, and we use standard image-processing techniques to determine, at all times, the mean concentration of the product in the system (which requires a calibration curve).

Before describing the chemical process, it is worth characterizing the chaotic nature of our system. Figure 2 shows a Poincaré map of the flow trajectories: One sees that the trajectories fill the regions outside the vortices and leave the vortex cores unvisited. As expected in a chaotic system, the trajectories of two particles initially adjacent diverge exponentially; typically, the rate of divergence is 0.04 s^{-1}.

Visualization studies performed with fluoresceine reveal striations developing in the regions outside the vortices. The evolution of their average thickness s versus time is shown in Fig. 3; one obtains an exponential decrease, at a rate equal to 0.11 s^{-1}. For the same period of time, the total area A of the concentration filaments and the mean concentration C
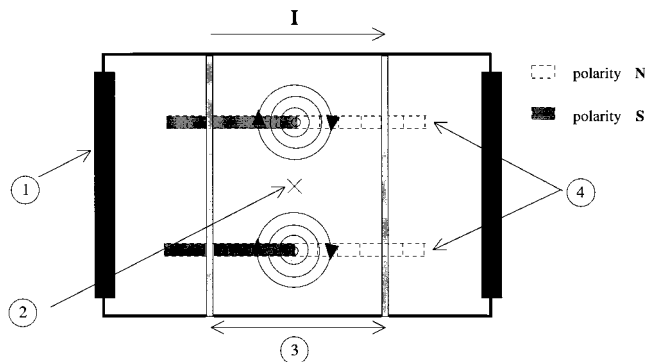

FIG. 1. Schematic representation of the experimental system: (1) electrode; (2) injection point of reactants (the reactants are injected with a burette whose end is connected to a fine tube); (3) studied region (observation zone); (4) configuration of the magnets. Each magnet produces a magnetic field which has a maximum value of 0.3 T and decays over a typical length of 3 mm.
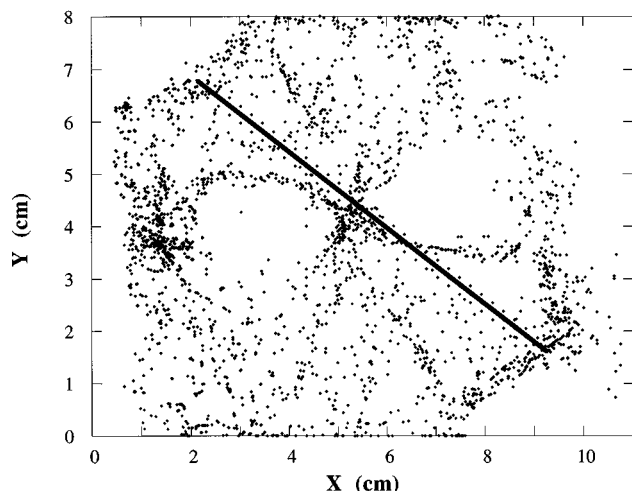
FIG. 2. Poincaré map of the flow trajectories. The positions of particles are taken at each period.

within them are roughly constant, as expected (Fig. 3). The small decrease of the concentration and the corresponding increase of the total area are due to diffusion (enhanced by the presence of small three dimensional recirculations within the layer). As C becomes roughly constant after a few periods, we consider that the concentration $C \sim 0.6 C_0$ is a reasonable estimate for the mean concentration in the striations.

III. RESULTS

Let us now study the chemical mixing. The first-order reaction we consider is the hydrolysis of the t-butyl chloride in the presence of NaCl, a well-documented reaction [10–12], which is expressed by the equation

$$(CH_3)_3CCl + H_2O \rightarrow (CH_3)_3COH + HCl.$$
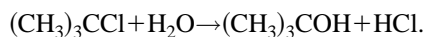
In the dilute case (here $[(CH_3)_3CCl] < 0.1$ mol), the reaction coefficient is independent of the initial concentration of t-butyl chloride [11]. The hydrolysis follows a first-order kinetics according to the law
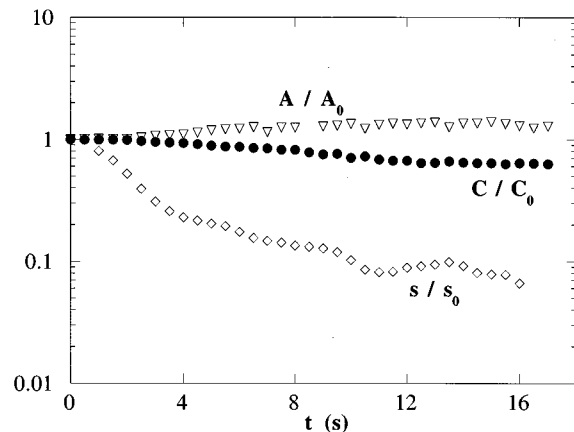

FIG. 3. Temporal evolution of the thickness of the striation s, of the total area A of the filaments, and of their mean concentration C. These quantities are renormalized by their initial values: ∇, A/A_0; $\bullet$, C/C_0; and $\diamond$, s/s_0.
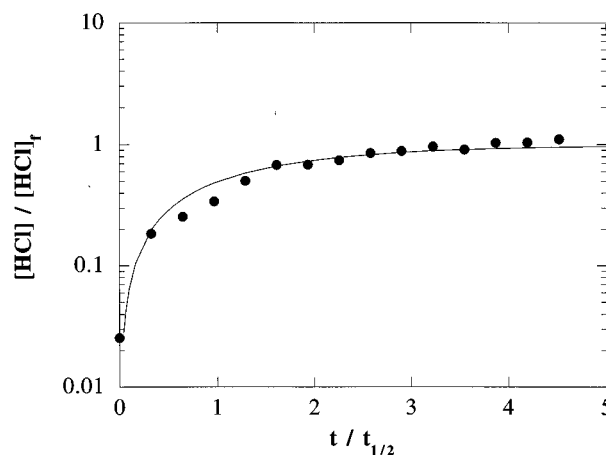

FIG. 4. Ratio of the concentrations $[HCl]/[HCl]_f$ as a function of $t/t_{1/2}$ ($[HCl]_f$ is the final concentration of HCl). Chaotic mixing (dots) and homogeneous mixing (solid line) are illustrated. The experimental error on the concentrations measurements is typically lower than 15%.

$$v_1(t) = \frac{d[HCl](t)}{dt} = k_1[(CH_3)_3CCl](t), \quad (1)$$

where $[\cdot]$ denotes the concentration and k_1 is the reaction coefficient experimentally determined. We find that $k_1 = 0.022 \text{ s}^{-1}$, which is consistent with previous determinations [10–12].

A drop of dilute $(CH_3)_3CCl$ initially is injected close to the hyperbolic point, and it is stretched and folded once per period of oscillation, so that after a few periods, the two reactants are entangled within each other. The mixing time t_M, taken as one period of oscillations, is 8 s in our case. It is interesting to follow the evolution of the averaged concentration of product [HCl], which is shown in Fig. 4; one observes that it increases with time and tends to reach an asymptotic value. Above a typical time, the reaction is achieved and the system does not evolve any more. Let us introduce a characteristic time of reaction t_R, taken as the half-life of the reaction $t_{1/2}$ and defined in this case by $t_R = \ln 2/k_1 \approx 32$ s and the Damköhler number $Da \equiv t_M/t_R$ [13,14], $Da \approx 0.22$ for this experiment. Since we are in a situation where the reaction time is larger than the mixing time and there is no nonlinearity in the kinetics of the reaction, we expect that the temporal evolution of the concentration will be the same as for a homogeneous mixing. This is precisely what we observe in Fig. 4.

Striking differences appear when we use a second-order reaction in the same flow and with comparable values of the Damköhler number. The corresponding reaction we consider here is the ionic reaction between the hydrogen peroxide H_2O_2, iodide ions I^-, and hydrogen ions H^+; the stoichiometric reaction reads

$$H_2O_2 + 2I^- + 2H^+ \rightarrow 2H_2O + I_2.$$

This reaction is also well documented [15]. When hydrogen is in excess, the concentration of H^+ remains essentially constant and the kinetics is governed by the equation

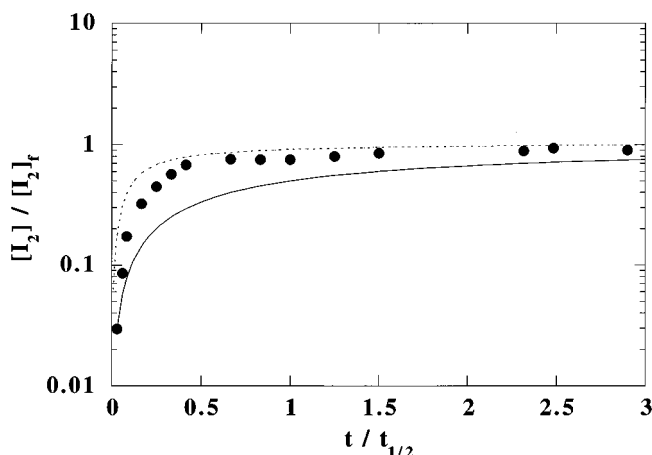$$v_2(t) = \frac{d[I_2](t)}{dt} = k_2[H_2O_2](t)[I^-](t), \quad (2)$$

FIG. 5. Ratio of the concentrations of $[I_2]/[I_2]_f$ as a function of $t/t_{1/2}$. Homogeneous mixing corresponds to the solid line, and formula (5) is displayed as a dashed line.

which is precisely a kinetics of second order. We have measured k_2 for a concentration $[H^+]=0.76$ mol which is the mean concentration (i.e., averaged throughout the reactor volume) we impose in the experiment, and we find $k_2 = 0.11$ mol^{-1} l s^{-1}. There is now a range of decay rates for the kinetics of the reaction: In the experiment, since $[H_2O_2]$ ranges between 0.33 mol (in the initial blob) and 0.0475 mol (when mixed with all the reactor), the chemical time constant lies between 13 and 96 s. The corresponding Damköhler numbers will therefore range between 0.6 and 0.08.

The temporal evolution of the concentration of iodine, obtained by doing the same experiment as above, but with the second-order reaction, is displayed in Fig. 5. One can see that the global reactivity is much larger than the one obtained by using homogeneous mixing. The typical time for the reaction is now 26 s (instead of 96 s for a homogeneous mixture). As already mentioned in the Introduction, the physical origin of this enhancement is that throughout the mixing process there exist sizable gradients of concentration. Kinetics is enhanced in regions of high concentrations of H_2O_2 and is slowed down in low-concentration regions. Since Eq. (2) is nonlinear, the reactivity is globally increased. For linear kinetics, such as the hydrolysis of the t-butyl chloride, there is no net effect on the global reactivity. To characterize the phenomenon by a number, one may determine an effective reaction coefficient k_{eff} obtained by assuming that the system is homogeneously mixed and the underlying reaction is of second order. We get $k_{\text{eff}}=3.8k_2$. There is thus an apparent enhancement of the reactivity, and it is permissible to say that chaotic stirring produces a ''dynamical catalytic effect.''

IV. DISCUSSION AND CONCLUSION

Here we offer a way to estimate the amplitude of the catalytic effect we introduced above. The starting point is to assume that the reaction takes place in the filaments, where the concentration (averaged over the total area occupied by the filaments) can be fitted by an expression of the form

$$[H_2O_2](t) = ([H_2O_2]_g - [H_2O_2]_m)e^{-t/\tau_D} + [H_2O_2]_m, \quad (3)$$

where $[H_2O_2]_g$ is the concentration in the initial blob, $[H_2O_2]_m$ the concentration averaged throughout the reactor, and τ_D the rate of decrease of $[H_2O_2](t)$ corresponding to Fig. 3. After integrating Eq. (2), we obtain that the global concentration of the formed product reads

$$[I_2](t) = \frac{[I^-]_0}{2}\left[1 - \exp\left(-2k_2\int_0^\infty [H_2O_2](t)dt\right)\right]. \quad (4)$$

We thus obtain for the global concentration of I_2 the expression

$$[I_2](t) = \frac{[I^-]_0}{2}\{1 - \exp[-2k_2(\tau_D\Delta(1-e^{-t/\tau_D})) + [H_2O_2]_m t]\}, \quad (5)$$

where $\Delta = [H_2O_2]_g - [H_2O_2]_m$.

This expression is represented in Fig. 5 (see the dotted line). Rough agreement is obtained between this line and the experiment. We find a characteristic reaction time $t_R=17$ s, to be compared to 26 s found experimentally. The reaction rate we find is thus 35% above the actual one; this deviation is significant, but, owing to the simplicity of the calculation, remains acceptable. Therefore, assuming that the reaction develops in the braids generated by the chaotic process allows us to determine effective reactivities consistent with the observations.

To summarize, we have shown, for a particular chaotic system and a second-order reaction, the existence of a catalytic effect which originates in the fact that concentration gradients persist as the chemical reaction proceeds. We have proposed a simple method to determine the global reactivity and have shown that the results agree, within 35%, with the experiment, whereas assuming homogeneous mixing leads to underestimate the reaction rate by a factor of 4. This approach underlines the role of the filaments produced by the chaotic process. More generally, one may expect that the dynamical catalytic effect is at work whenever a chemical reaction with nonlinear kinetics (non-necessarily of second order) takes place in a chaotic flow, provided the Damköhler number is neither too small nor too large. In the series of experiments we have performed with the second-order reaction, the overall Damköhler number ranges between 0.08 and 0.6. In the arctic pole, the set of reactions leading to ozone destruction defines a complex chemical system, but its kinetics is close to that of a second-order reaction [16]. The corresponding overall Damköhler number estimated from stratospheric data [17–19] is roughly 0.02; this is on the border of the range we have considered in our experiment. Thus one may suggest that the catalytic effect we discuss here is at work and, therefore, may contribute to increase the rate at which the ozone is destroyed in the arctic pole, as proposed in [6].

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