Transitions in two-dimensional patterns in a ferrocyanide–iodate–sulfite reaction

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Transitions in two-dimensional (2D) spatial patterns were investigated in a ferrocyanide–iodate–sulfite (FIS) reaction in a circular thin gel reactor. The state of the gel reactor was maintained by contact of one side of the gel with a continuously refreshed well-stirred reservoir. For long residence times of the chemicals in the reservoir, the gel reactor was in a spatially uniform state of low pH (about 4), while at short reservoir residence times the reactor was in a uniform state of high pH (about 7). At intermediate residence times the spatiotemporal 2D structures observed include a large low pH oscillating spot, small metastable high pH oscillating spots, shrinking rings, spirals that formed when the axisymmetry of shrinking rings was broken, self-replicating spots that either grew and divided or died from overcrowding, and highly irregular, stationary lamellae. Transitions among the different patterns were examined as a function of gel thickness (0.2–0.6 mm), reservoir residence time (0.6–4 min), and ferrocyanide concentration (12–80 mM). Iodate and sulfite concentrations were held fixed at 75.0 and 89.0 mM, respectively. Several transitions were examined in detail: from a stationary spot to an oscillating spot; from an oscillating spot to a shrinking ring or spirals; the onset of replicating spots; and the transition from a homogeneous state to lamellar patterns. The observed phenomena can all be described in terms of a parity-breaking front bifurcation (nonequilibrium Ising-Bloch bifurcation).

I. INTRODUCTION

Pattern formation in a reaction-diffusion system arises from the interplay of local chemical dynamics and diffusive transport.\textsuperscript{1,2} Transitions from a homogeneous state to a state of spatial patterns can arise from a local instability in a homogeneous steady state; examples include Turing patterns in the chlorite–iodide–malonic acid (CIMA) reaction\textsuperscript{3–6} and spiral phase waves in the Belousov-Zhabotinsky (BZ) reaction.\textsuperscript{7,8} Transition to a pattern can also arise from a global instability due to the interplay of multiple homogeneous steady states and diffusion; examples include spiral excitable waves in the BZ reaction\textsuperscript{9–13} and pattern formation near a nonequilibrium Ising-Bloch bifurcation in the ferrocyanide–iodate–sulfite (FIS) reaction.\textsuperscript{14–16} While Turing patterns in the CIMA reaction and spirals in the BZ reaction are well documented, pattern formation near a nonequilibrium Ising-Bloch bifurcation, which is the subject of the present study, has been only recently observed.\textsuperscript{14–18}

We examine pattern formation in a FIS reaction in a quasi-two-dimensional open reactor. Our study focuses on the bistable regime where two homogeneous regions can coexist with a sharp chemical front separating the two regions. Analyses of a bistable reaction-diffusion model by Hagberg and Meron\textsuperscript{19–22} show that a variety of patterns can form near a parity breaking bifurcation (nonequilibrium Ising-Bloch bifurcation),\textsuperscript{19,23} where a single chemical front bifurcates into two counter propagating fronts. Figure 1 presents some patterns observed in the neighborhood of a transition that we interpret to be a nonequilibrium Ising-Bloch bifurcation. An extrinsic perturbation (e.g., by a boundary) or an intrinsic perturbation (e.g., a curvature effect) can lead to oscillations in the size of a spot; Fig. 1(a) shows an example of such a breathing spot. In the Bloch regime beyond the nonequilibrium Ising-Bloch bifurcation we observe shrinking rings [Fig. 1(b)] and spirals [Fig. 1(c)]. Self-replicating spots [Fig. 1(d)] arise from a transverse instability of a chemical front; this instability can also lead to stationary lamellar patterns, as illustrated in Figs. 1(e)–1(f).

We will summarize our observations in two phase diagrams where the relations among different patterns can be identified and transitions from one state to another can be understood. The observed transitions, interpreted in terms of the nonequilibrium Ising-Bloch bifurcation, elucidate the behavior of self-replicating spots, spirals, and lamellar patterns, which were initially studied by Lee et al.,\textsuperscript{14–16} and the behavior of oscillating spots and shrinking rings, which were discovered by Haim, Li, and co-workers.\textsuperscript{18} We report here a new type of breathing spot due to a curvature effect discussed by Hagberg and Meron,\textsuperscript{24} and we describe the mechanism of the transverse instability observed in the process of spot replication.

Section II introduces the experimental setup and the chemical system used in this study. Section III presents the phase diagrams, describes each type of pattern observed, presents quantitative results for several transitions from one type of pattern to another, and compares the observations with the theory of Ising-Bloch bifurcation. Section IV contains our conclusions.

II. EXPERIMENTAL SYSTEM

The reactor and optical system used in the present experiments are similar to those used by Lee et al.\textsuperscript{14–16} The
reaction medium is a transparent polyacrylamide gel,\textsuperscript{16} 22.0 mm in diameter and 0.2–0.6 mm thick. The gel allows reaction and diffusion processes to occur but prevents convection. One side of the gel membrane is fed diffusively through contact with a continuously refreshed stirred reservoir (2.8 m/s) of the FIS chemicals. Four precision Pharmacia piston pumps first feed the chemicals into a vigorously stirred premixer (1.0 m/s) in two streams: one with H\textsubscript{2}SO\textsubscript{4} and NaIO\textsubscript{3}, the other with Na\textsubscript{2}SO\textsubscript{3} and K\textsubscript{4}Fe(CN)\textsubscript{6}·3H\textsubscript{2}O. The FIS reaction takes place in the premixer and the reservoir and also in the tubes connecting the premixer to the reservoir (total volume of the system = 4.0 m\textsuperscript{3}). Flow rate stability (0.2\% during the course of an experiment) and reproducibility (0.2\%) are important because the pattern dynamics is very sensitive to the flow rate of the reservoir. The precision flow control maintains the reservoir in a well-defined nonequilibrium state that serves as a time-independent homogeneous boundary condition for the gel. The whole system is immersed in a temperature-controlled water bath (30.0 ± 0.1 °C).

The gel reactor is illuminated by light at a wavelength (420 ± 20 nm) that is absorbed mainly by ferrocyanide.\textsuperscript{16} Images of reflected light are obtained with a monochrome video camera (MTI CCD72), digitized by a frame grabber (Data Translation DT2853) with a spatial resolution of 512 × 480 pixels, and stored in a computer for further analysis. In the images a low pixel value represents high ferrocyanide concentration, low pH (about 4), and the oxidized state of the reaction system, while a high pixel value represents low ferricyanide concentration, high pH (about 7), and the reduced state of the reaction system.

For a wide parameter range the FIS reaction in a stirred flow reactor has two stable states, one with high pH and one with low pH. In all of the present experiments the stirred reservoir is maintained in the high pH state. The reservoir flow rate,\textsuperscript{25} the gel thickness, and the ferrocyanide concentration are used as the control parameters; other conditions are kept constant. Stock solutions of NaIO\textsubscript{3} (Aldrich), Na\textsubscript{2}SO\textsubscript{3} (Sigma), K\textsubscript{4}Fe(CN)\textsubscript{6}·3H\textsubscript{2}O (Sigma), and H\textsubscript{2}SO\textsubscript{4} (EM Science) are prepared with doubly distilled water, and their concentrations are determined by the weights of the dissolved chemicals.

III. PATTERNS AND BIFURCATIONS

The phase diagram in Fig. 2(a) shows the regimes for the different patterns observed as a function of gel thickness and reservoir flow rate. Detailed bifurcation diagrams for 0.3 mm and 0.2 mm thick gels are shown in Figs. 3(a) and 3(b), respectively. Figure 2(b) shows how the different regimes depend on ferrocyanide concentration and flow rate. These phase diagrams were all obtained as a function of flow rate with other parameters held fixed during each scan. No hysteresis was observed in scans made with increasing and de-


diagram adapted from J. Chem. Phys., Vol. 105, No. 24, 22 December 1996

FIG. 1. Snapshots of some spatial patterns observed in the FIS reaction. (a) Oscillating spot. The size of the spot increases and decreases periodically. (b) Shrinking ring. The black ring shrinks and disappears in the center while a new ring appears near the boundary. (c) Rotating spirals. (d) Self-replicating spots. (e) Stationary lamellar patterns. Each picture is 20 mm in diameter; the behavior near the gel rim is different from that in the central region because the rim of the gel is in contact with the gel holder and not the reservoir. For the different patterns the gel thickness (mm), [Fe(CN)\textsubscript{6}^4\textsuperscript{-}]\textsubscript{0} (mM), and flow rate (m/s/h) are: (a) 0.3, 20, 160; (b) 0.3, 20, 280; (c) 0.3, 20, 360; (d) 0.2, 20, 148; (e) 0.2, 20, 136; (f) 0.3, 16, 180. In all of the experiments in this paper the following conditions are fixed: [NaIO\textsubscript{3}]\textsubscript{0} = 75.0 mM, [Na\textsubscript{2}SO\textsubscript{3}]\textsubscript{0} = 89.0 mM, [H\textsubscript{2}SO\textsubscript{4}]\textsubscript{0} = 3.35 mM, and temperature = 30.0 ± 0.1 °C. ([p]\textsubscript{0} denotes the value of a reactant concentration in the reservoir before any reaction takes place.)
increasing flow rate for 0.3 mm and thicker gels, while hysteresis was observed for the 0.2 mm thick gel [cf. Fig. 3(b)].

The role of gel thickness is discussed in the following subsection. The subsequent discussion and all figures other than Fig. 2(a) present results for either a 0.3 mm thick gel [Figs. 1(a)–1(c), 1(f), 2(b), 3(a), and 4–7] or a 0.2 mm thick gel [Figs. 1(d)–1(e), 3(b), and 8–13].

After discussing the dependence on gel thickness, we will describe each type of pattern and some of the transitions among them. These studies were all made with [Fe(CN)₆]₄⁻_0 = 20 mM, except for Fig. 1(f) and Fig. 2(b).

A. Dependence of patterns on gel thickness

Patterns are observed only for gels between about 0.2 mm and 0.6 mm thick [cf. Fig. 2(a)]. For gels of 0.6 mm or greater thickness, only the spatially uniform low pH (black) state is stable, while for gels less than about 0.2 mm thick, the uniform high pH (white) state is observed. Patterns form only for a certain range of gel thickness because they arise as a result of evolution and interaction of chemical fronts, which exist only when the system is bistable. In a continuous flow stirred tank reactor the FIS reaction is bistable for a certain range of residence times—for long residence times only the low pH state is stable, while for short residence times only the high pH state is stable. The residence time in a gel increases with increasing thickness of the gel. Thus for gels 0.6 mm thick or thicker, the residence time in the gel is apparently too long for the reaction to be bistable—only the low pH state is stable. For gels less than 0.2 mm thick, the residence time in the gel is too short for the reaction to be bistable—only the high pH state (the state of the stirred reservoir) is stable.

B. Large oscillating low pH spot

1. Observations

Figure 4 presents an example of an oscillating spot—the large black spot periodically grows and shrinks, oscillating in size with constant amplitude (5.5 mm variation in diameter) and period (18.5 min). At the beginning of the experiment, starting from low flow rate, a small black spot appears spontaneously near the center of the gel. It grows gradually in time while becoming axisymmetric. When the black front approaches the reactor boundary, it slows down and stops,
thus forming a large stationary black spot. At a sufficiently high flow rate the convergence to a stationary spot is accompanied by damped oscillations. If the flow rate is increased beyond a critical value (158 m/s), the stationary low pH spot, shown in one-dimensional time evolution of a cross section of the spot in Fig. 5(a), becomes unstable and spontaneously begins to oscillate, as shown in Fig. 5(b). Near onset the front oscillations have a small amplitude and are nearly sinusoidal [Fig. 5(b)], while far above onset, the oscillations have large amplitude and have a relaxational form [Fig. 5(c)]. When the spot expands from minimum, the wave front is slightly distorted away from its circular shape. As the front approaches the reactor boundary, the spot regains its axisymmetry.

The phase portrait formed by plotting the front velocity as a function of the distance of the front from the reactor wall is a limit cycle, as Figs. 6(a) and 6(b) illustrate. The front velocity was obtained from the difference in the front position in frames 30 s apart. Positive velocity is defined as the direction of the black state invading the white state. Just beyond the onset of oscillations, the limit cycle is small and symmetric about the axis \( v = 0 \) [Fig. 6(a)], while well above the transition the limit cycle becomes asymmetric [Fig. 6(b)]. The speed of the expanding front is larger than the speed of the shrinking front.

To determine the type of bifurcation we measured the amplitude of oscillations \( A \), defined as the difference between the maximum and minimum distance of the black-white front from the reactor wall, as a function of a control parameter, the flow rate. Figure 6(c) shows that \( A^2 \) increases linearly from zero as the flow rate passes the onset of oscillations, which indicates that the bifurcation is a supercritical Hopf bifurcation.

2. Interpretation

Oscillating spots were predicted in earlier numerical and analytical studies of an activator-inhibitor model by Hagberg and Meron.\(^{20–22}\) When the system is in the bistable regime, the states corresponding to the black and white states in our experiments are each stable and can coexist in different spatial regions with a front separating them. Motion of the front can be unidirectional, corresponding to an Ising front, e.g., the black state invades the white state; this is called a black-white front. Or the motion can be bidirectional with two “Bloch” fronts (a black-white front and a white-black front). Elphick et al.\(^{22}\) found that on approach to the non-equilibrium Ising-Bloch bifurcation (from the Ising regime), the monotonic relation between front velocity and perturbation parameters becomes multivalued and the stationary front is destabilized, resulting in a state with an oscillating front.

The transition sequence of Fig. 5 can be interpreted in terms of the Ising-Bloch bifurcation as follows: below the bifurcation (flow rate < 158 m/s), only the black-white front exists. As the black-white front approaches the boundary, it interacts with the boundary, slows down, and stops at a finite distance from the boundary, resulting in a stationary black spot.\(^{18}\) When the flow rate is increased to the vicinity of the Ising-Bloch bifurcation (160–240 m/s), a white-black front co-exists near the reactor boundary. The black-white front is selected when the front is far from the boundary, and the black spot then grows, but as this front approaches the boundary, the white-black front becomes preferred, leading to a reversal of the front propagation direction and to a shrinking of the spot until the white-black front becomes unstable. Thus the oscillations of Figs. 5(b)–5(c) can be regarded as periodic transitions between white-black...
and black-white propagating fronts. Far beyond the Ising-Bloch bifurcation, the white-black front exists everywhere in the reactor; hence when the black-white front approaches the boundary and rebounds, the white-black front persists until it disappears in the center of the reactor—examples of the resulting shrinking ring patterns, which are the subject of the next subsection, are shown in Figs. 5(e) and 5(f).

C. Shrinking rings and spirals

When the flow rate is increased in the regime of oscillating low pH spots, there is a transition marked by the periodic emergence of black rings near the edge of the reactor, as shown in Figs. 5(d)–5(f). The outer front of the ring travels toward the boundary, stops, rebounds, and begins to shrink, while the inner front shrinks and catches up with the collapsing black spot [see Fig. 5(d)]. With further increase in flow rate, each black spot completely collapses and disappears in the center, while a new black ring simultaneously emerges near the boundary; this periodic process is illustrated in Figs. 5(e) and 5(f).

At yet higher flow rate (or at high ferrocyanide concentration), the shrinking rings are not precisely axisymmetric. When the axisymmetry is broken, the system generates pairs of defects that organize spiral waves and serve as spiral centers. Figure 7 presents a time sequence of spiral waves with two spiral centers. The number of spiral centers observed in our experiments ranged from two to six.

D. Small oscillating high pH spots

1. Observations

In the parameter range with a large low pH spot (Sec. III B), we find that local perturbations (e.g., briefly stopping the stirring of reservoir) of this black spot can produce small oscillating high pH (white) spots within the large spot, as Fig. 8 illustrates. The spots are metastable, lasting for a few hours (typically 20 oscillations) before disappearing.

2. Interpretation

The oscillating small white spots, like the oscillating large black spots (Sec. III B), can be explained in terms of the nonequilibrium Ising-Bloch bifurcation theory. In both cases the oscillations correspond to periodic transitions between white-black and black-white propagating fronts. However, for the black spots the transition arises from interaction of the front with the boundary, while for the white spots the transition arises from the effect of curvature. (The axisymmetry of the white spot in Fig. 8 throughout the oscillation cycle indicates that the effect of the boundary on the spot is small; our discussion assumes the boundary effect to be negligible.)

Figure 9 shows the limit cycle formed by plotting the front velocity of the white spot as a function of the spot curvature. For large front curvature (> 1.8 mm⁻¹), only the white-black front exists, while for small front curvature (< 1.4 mm⁻¹), only the black-white front exists, (cf. Sec. III B). For intermediate values of curvature (1.4–1.8 mm⁻¹), the front velocity is multivalued. When the spot shrinks (due to the movement of black-white front) to a critical curvature value (1.8 mm⁻¹), the black-white front becomes unstable and undergoes a transition to white-black

FIG. 7. A time sequence of a spiral pattern with two spiral tips, which are generated when the shrinking ring pattern loses axisymmetry. The flow rate is 360 m/h and the gel thickness is 0.3 mm [as in Fig. 1(c)]. Each picture is 20 mm in diameter.

FIG. 8. An oscillating metastable high pH (white) spot within a low pH (black) spot. (a) Image of the entire gel reactor (22 mm diameter), showing the size and location of the oscillating high pH spot (highlighted with a box). (b) Time sequence of images (1.9×1.9 mm²) of the oscillating spot. The oscillations are induced by curvature of the chemical front (cf. Sec. III D 2). (c) Spot diameter as a function of time. The flow rate is 120 m/h and the gel thickness is 0.2 mm.
front, and the spot size begins to increase. When the spot increases to another critical curvature value (~1.4 mm$^{-1}$), there is a transition from the white-black front to the black-white front, and the spot begins to shrink. Thus as in the case of the black spots, the oscillations correspond to periodic transitions from black-white to white-black fronts.18,22

E. Self-replicating spots and lamellae

1. Observations

Replicating spots and lamellae were found in the FIS reaction by Lee et al.14–16 Here, we describe the phenomena and propose an interpretation in terms of a transverse front instability. Figure 10 illustrates the spot replication process. Small white spots were formed initially by a perturbation (briefly stopping the stirring of the reservoir) in the parameter regime where there is a large oscillating black spot. A new-born spot shrinks and dies if it is very crowded by neighboring spots; if the spot is a little less crowded, it first shrinks slightly and then begins to grow. The growth of a spot is anisotropic (e.g., see the spot at 4.5 min in Fig. 10) because of interaction with neighboring spots. Later in the growth process, the middle part of the spot starts to shrink, creating a spot with a peanut shape (e.g., at 8.0 and 9.5 min in Fig 10). Eventually a peanut-shaped spot splits into two smaller spots at the point of most negative curvature (e.g., at 10 min in Fig. 10), and the two spots move away from each other (at 11 min in Fig. 10). Nearby spots can grow towards one another but never collide. Occasionally an elongated spot divides into three or more spots. Asymptotically the black domain is filled by white spots.

If the perturbation generates a few large white domains rather than many small white spots, these domains gradually elongate to fill the black region, developing a lamellar pattern like that shown in Fig. 11 (0 min). The white-black fronts grow fast where the curvature is large and grow slowly or stop growing where the curvature is smaller (Fig. 11 at 30 and 60 min). Fronts propagating towards one other reach a minimum separation, then bounce back slightly. Finally, the black domain is covered by white bands with black filaments between them (Fig. 11 at 90 min); there is no further evolution of the basic pattern but there is a very slow drift over a long time scale.

The bifurcation diagram in Fig. 3(b) shows that there is a parameter range with coexisting replicating spots, lamellae, the large black (low pH) oscillating spot, and the homogeneous white (high pH) state. At low flow rate (120 m$/$h), small white spots generated by a perturbation gradually shrink and finally disappear, as Fig. 12 illustrates.

Above a critical flow rate value (124 m$/$h), small white spots generated by a perturbation evolve into self-replicating spots, as Fig. 10 illustrates. In the same flow rate range, a perturbation generating large white spots leads to a lamellar pattern (cf. Fig. 11). If the flow rate is reduced when there is a lamellar pattern, below a certain value (128 m$/$h), the white bands shrink in length and width and then disappear in the black background. Similarly, if the flow rate in the lamellar regime is increased beyond 160 m$/$h, the black filaments shorten and break, leading to a uniform high pH state.14,16

2. Interpretation

We now show that the self-replicating spot phenomenon can be interpreted as arising from a transverse instability in the chemical front.19–21,27–29 The velocity of a chemical front in a two-dimensional system can be written as
v_n = v_0 - D_e \kappa, \text{ to lowest order in } \kappa, \text{ where } v_n \text{ is the normal velocity of the local front, } v_0 \text{ is the velocity of a planar front, } \kappa \text{ is the curvature of the front, and } D_e \text{ is a constant, an effective diffusivity.}^{20,21} \text{ If } D_e > 0, \text{ the local velocity of the front is smaller in a region of large curvature than it is in a region of small curvature. Consequently, any variation of curvature on the front will decrease as the front evolves; thus the front is transversely stable. On the other hand, if } D_e < 0, \text{ the local velocity of the front is larger in a region of large curvature than it is in a region of small curvature. Thus curvature variations are amplified and the front is unstable.}

Figure 13 shows measurements of the local velocity as a function of curvature of the front for two cases, one for a flow rate \approx 120 m/l/h; solid line and for the replicating spot in Fig. 10 (dashed line). The negative slope of the graph for the spot in Fig. 12 indicates that the effective diffusivity for this case is positive; hence the spot is transversely stable. In contrast, the positive slope for the replicating spot in Fig. 10 indicates that the effective diffusivity is negative and hence the spot is transversely unstable. The uncertainty in the curvature determination is \pm 0.5 mm^2; the uncertainty in the velocity is 0.04 mm/min.

**FIG. 11.** Development of a lamellar pattern following a perturbation of the black (low pH) state. The asymptotic state is reached in about 90 min. The flow rate is 136 m/l/h and the gel thickness is 0.2 mm [as in Fig. 1(e)]. Each picture is 20 mm in diameter.

**FIG. 12.** The time evolution of white spot following a finite perturbation shows that the spot is transversely stabilized by curvature. The spot eventually disappears at long times (several hours). The flow rate is 120 m/l/h and the gel thickness is 0.2 mm (as in Fig. 8). Each frame is 2.5\times2.5 mm^2.

**FIG. 13.** The front velocity measured as a function of front curvature for the metastable spot in Fig. 12 (solid line) and for the replicating spot in Fig. 10 (dashed line). The negative slope of the graph for the spot in Fig. 12 indicates that the effective diffusivity for this case is positive; hence the spot is transversely stable. In contrast, the positive slope for the replicating spot in Fig. 10 indicates that the effective diffusivity is negative and hence the spot is transversely unstable. The uncertainty in the curvature determination is \pm 0.5 mm^2; the uncertainty in the velocity is 0.04 mm/min.

**IV. DISCUSSION**

We have examined pattern formation near the nonequilibrium Ising–Bloch bifurcation with the FIS reaction in a quasi-two-dimensional open reactor. The phase diagrams built in this work provide insight into the individual patterns and the transitions between patterns, and offer a direct comparison with the model studies conducted by different groups (Hagberg and Meron,^{19–22,24,26} Osipov and co-workers,^{30–32} and others^{33–35}). In this report, we mainly compared our experimental results with Hagberg and Meron’s analyses of the nonequilibrium Ising–Bloch bifurcation.^{19–22} A typical transition sequence observed with increasing flow rate for gels at least 0.3 mm thick is uniform low pH state \rightarrow stationary low pH state.
pH spot → oscillating low pH spot → shrinking rings or spirals → uniform high pH state. The transition from a stationary spot to an oscillating spot is due to an extrinsic (e.g., boundary effect) or intrinsic (e.g., curvature) perturbation that occurs near but before an Ising-Bloch bifurcation. In this regime the relation between front velocity and perturbation is multivalued for a certain range of perturbation values, and the oscillating spot is a result of periodic transitions between white-black and black-white propagating fronts. The transition from an oscillating spot to a shrinking ring or spirals occurs at the onset of the Ising-Bloch bifurcation, where the white-black front is stable everywhere; the transition from white-black to black-white front is then not possible, and the white-black front collapses in the center of the reactor and disappears.

In a thinner gel (0.2 mm), a typical sequence with increasing flow rate is uniform low pH state → oscillating low pH spot → (with a finite perturbation) self-replicating spots or lamellae → uniform high pH state. The replicating spots arise from a transverse instability—fluctuations in curvature are amplified. In this transversely unstable case the fixed point (zero velocity) has positive curvature, as shown in Fig. 13. Hence, neglecting lateral perturbations, there should exist a state with stable spots of a fixed finite size—spots with a larger size will shrink and spots with a smaller size will grow. If the interaction of the chemical fronts of different spots then suppressed the lateral instability, the spots could form an ordered array (e.g., a hexagonal pattern). The numerical simulation of Pearson revealed this possibility, but we have not found such patterns in our experiments on the FIS reaction.

Middya and Luss have found that global coupling can play a role in experiments with the type of reactor that we have used. Indeed, some global coupling is always present in this geometry (although it can be reduced by increasing the flow rate and/or using smaller reservoirs). While we cannot completely dismiss the possible role of global coupling in the present experiments, to check for this possibility we monitored reservoir pH; the absence of any time dependence in the pH indicates that global coupling effects are secondary.

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25. The reactor resident time (τ) can be calculated from the reactor flow rate (f) and the reactor volume (V) using τ = V/f.