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Logical Functions of a Cross Junction of Excitable Chemical Media

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We discuss properties of a cross junction composed of active areas, in which the Belousov−Zhabotinsky reaction proceeds, and passive stripes. The response of such a junction with respect to pulses of excitation arriving from perpendicular directions is studied. It is shown that the device works as a coincidence detector because the second pulse is stopped if it arrives earlier than a certain characteristic time after the first one. Using the Rovinsky−Zhabotinsky model, we calculate the size of the cross junction and specify its temporal characteristics. We suggest how the cross junction can work as a switch of a chemical signal.

Introduction

The idea of information processing with purely chemical devices is attractive both as an interesting scientific question and because of its potential technological applications. Various theoretical studies and experiments related to this problem have been reported in recent years. They include successful applications of chemical waves in image processing for both contrast and contour analysis presented in ref 1. Another class of chemical devices that process information utilize the fact that a chemical pulse, which can be produced in excitable or oscillatory media, carries information. The area of a high concentration of a particular reactant may be considered as corresponding to the logical "true" state, while the area of a low concentration corresponds to the logical "false". Using this idea the chemical reactors that work as the simplest logical gates (AND, OR, NOT) were constructed.[2,3]

It has been found[4] that a chemical system may perform more complex logical operations if it is inhomogeneous and composed of "active" regions, in which reactions occur, and "passive" areas, where some of the reagents are absent and so only part of reactions proceed there. In practice it means that an immobilized catalyst is inhomogeneously distributed in space. The passive areas are those which do not contain catalyst. In the following we discuss results obtained for such reaction scheme that the system is in an excitable state within the active regions.

Let us consider two active areas separated by a stripe of the passive one. A pulse of excitation propagating in one of these areas may excite the other active area if the passive stripe is narrow. The maximum width of the passive stripe for which such excitation still occurs is called the penetration depth. It has been found that the penetration depth depends on the geometry of the junction and on the direction of propagation of the excitable pulse.[4] Therefore the topology of a reactor, its geometrical size, and the directions of incoming chemical "signals" imply its logical functions. A few particular arrangements of active and passive fields have been studied, and such devices as a chemical diode[4−7] and a chemical memory, which can be written, read, and erased, have been constructed.[4] The predictions of the theory[5] have been nicely confirmed by working experimental setups.[6,7]

In our recent work[8] we have studied the properties of a plane (two-dimensional) system, composed of active (excitable) and passive (diffusion) areas in which no reaction occurs and only one of the reagents (u) can diffuse. In the active areas the system's dynamics was described by a simple FitzHugh−Nagumo type model:[4,9,10]

$$\tau\frac{\partial u}{\partial t} = -\gamma[ku(u-\alpha)(u-1)+v] + D_{\mathrm{u}}\nabla^2 u \qquad (1)$$

$$\frac{\partial v}{\partial t} = \gamma u \qquad (2)$$

with the parameters given by Motoike and Yoshikawa in ref 4. In eqs 1 and 2 the value $\gamma = 1$ corresponds to active regions and $\gamma = 0$ to passive ones. Such model uses a simplified version of FitzHugh−Nagumo dynamics originally introduced to describe excitable behavior of nerve tissues. This dynamics reflects the basic features of an excitable system, so it has been used as a generic model for nonlinear chemical phenomena.[11] However, because the values of the variables may be negative, their association with concentrations of reagents is not direct. Thus, the calculations based on eqs 1 and 2 can give the qualitative information on system's evolution only.

In ref 8 we have considered a junction of two perpendicular channels, as shown on the scheme in Figure 1, where the thick black lines stand for the stripes of diffusion field and the white areas 1−9 are the active regions. We have investigated the response of such system with respect to pulses coming from perpendicular directions (e.g. areas 4 and 8 in Figure 1) by solving numerically the reaction−diffusion eqs 1 and 2. The width of the diffusion stripes has been selected in such a way that a single pulse propagating in one of the channels is not able to move "sideways" because the width of the stripe of the diffusion field is larger than the penetration depth for a pulse moving parallel to the interface of active and passive regions. On the other hand, the width of the diffusion stripes is smaller than the penetration depth for a pulse perpendicular to the interface, so the pulse can propagate through such stripe.

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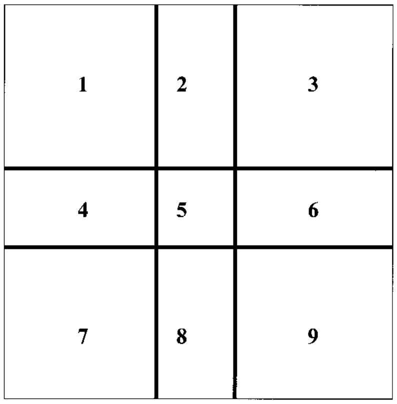

Figure 1. Geometry of the considered cross junction device: white areas correspond to the excitable field and the darker stripes to the diffusion one. The excitable areas are numbered to simplify their description in the text.

It is obvious that a cross junction of excitable areas with the geometry shown in Figure 1 works as a coincidence detector of the incoming pulses. If the moments of their arrivals to the central field are well separated, they do not interact and each of them follows its own path. On the other hand, if the later of the pulses arrives just after the first one, it finds the central part in a refractory regime. Therefore the central field cannot be excited and so the pulse is stopped. However, for a certain range of the time difference between arriving pulses, we observed an additional interesting phenomenon presented in Figure 2A−C.[8] When the second of the incoming pulses arrives (in the presented case after $\Delta t = 4.64$), it finds the central field inhomogeneously relaxed. The left-hand side of the central field, from which the first of the pulses entered, may be excited easier than the right-hand side one. As the result, the excitation of the central area by the second pulse has a radial shape originating from the bottom left corner (see Figure 2B). When this excitation arrives at the boundaries of fields 2 and 6 (in Figure 1), it is almost perpendicular to the passive stripes and so it is able to get through them. As the result the pulse duplicates creating two pulses propagating in fields 2 and 6 (see Figure 2C).

The motivation for this work was to check whether such switch of a chemical signal can be constructed on the basis of an excitable chemical system with the ferroin-catalyzed Belousov−Zhabotinsky reaction (B−Z).[12] We present the results obtained for the Rovinsky−Zhabotinsky model of the B−Z reaction[13,14] and estimate the size of the system and its temporal characteristics. Our calculations indicate the potential experimental difficulties which can appear when one tries to realize a cross junction with the properties discussed above in a laboratory.

Cross Junction of the Excitable System with the Belousov−Zhabotinsky Reaction

In this section we discuss the properties of a cross junction of active and passive fields, arranged as shown in Figure 1 in the case of dynamics corresponding to the Belousov−Zhabotinsky reaction (B−Z). We study the results of this system with respect to pulses coming from the perpendicular directions. The propagation of pulses is calculated using the Rovinski−Zhabotinsky model of the Belousov−Zhabotinsky reaction.[13,14] The model is based on the Field−Körös−Noyes[15,16] mechanism of the Belousov−Zhabotinsky reaction[14] completed by the hydrolysis of bromomalonic acid to tartronic acid.[13] In the Supporting Information we repeat the calculations, which show how to transform the original five variable model into the simplified, two variable one.

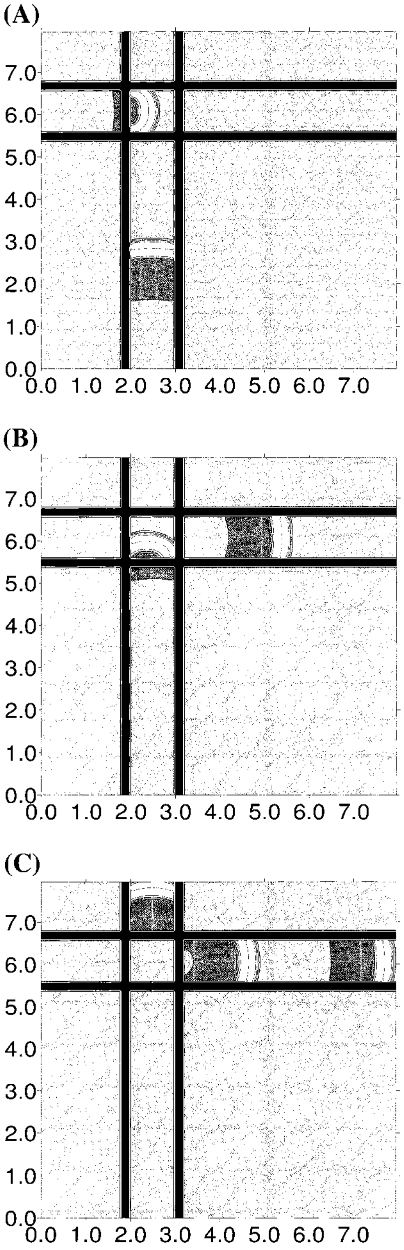

Figure 2. Switching behavior of a cross junction in the FitzHugh−Nagumo model. The figures show the time evolution of the concentration of activator in the case the second pulse of excitation arrives $\Delta t = 4.64$ after the first one. The lighter areas correspond to higher concentration. (A) $t = 4.0$. The first pulse arrives at the central field. (B) $t = 8.5$. The second pulse is asymmetrically generated in the central area. (C) $t = 11.5$. The second pulse splits into two, propagating in areas 2 and 6.

The Rovinsky−Zhabotinsky model uses two variables, x and z, corresponding to dimensionless concentrations of the activator $HBrO_2$ and of the oxidized form of catalyst $Fe(phen)_3^{3+}$. In the active regions, which contain the catalyst, the time evolution of the concentrations of x and z is described by eqs 3 and 4:

$$\frac{\partial x}{\partial \tau} = \frac{1}{\epsilon}\left[x(x-1) - \left(2q\alpha\frac{z}{1-z} + \beta\right)\frac{x-\mu}{x+\mu}\right] + \nabla_\rho^2 x \qquad (3)$$

$$\frac{\partial z}{\partial \tau} = x - \alpha\frac{z}{1-z} \qquad (4)$$

In the passive regions, without catalyst, the concentrations of x

and z evolve according to eqs 5 and 6:

$$\frac{\partial x}{\partial \tau} = -\frac{1}{\epsilon}\left[x^2 + \beta\frac{x-\mu}{x+\mu}\right] + \nabla_{\rho}^{2} x \tag{5}$$

$$z = 0 = \text{constant} \tag{6}$$

All variables and coefficients in eqs 3−6 are dimensionless. The real concentrations of $HBrO_2$ and $Fe(phen)_3^{3+}$ (X, Z) are related to (x, z) in the following way:

$$X = \frac{k_1 A}{2k_4} x \tag{7}$$

$$Z = Cz \tag{8}$$

The coefficients α, β, μ, and ϵ are defined as

$$\alpha = \frac{k_4 K_8 B}{k_1^{\,2} A^2 h_0^{\,2}} \tag{9}$$

$$\beta = \frac{2k_4 k_{13} B}{k_1^{\,2} A^2 h_0} \tag{10}$$

$$\mu = \frac{2k_4 k_7}{k_1 k_5} \tag{11}$$

$$\epsilon = \frac{k_1 A}{k_4 C} \tag{12}$$

where $k_{\pm i}$ denote the rate constants of the corresponding reactions in the Field−Körös−Noyes model[13−16] and A = [$HBrO_3$], B = [$CHBr(COOH)_2$], C = [$Fe(phen)_3^{2+}$] + [$Fe(phen)_3^{3+}$], R = [$\cdot CBr(COOH)_2$], U = [$HBrO_2^{+}$], X = [$HBrO_2$], Y = [Br^-], Z = [$Fe(phen)_3^{3+}$], and q is the stoichiometric factor. Parameter h_0 denotes the Hammett acidity function, describing the effective proton concentration,[17−19] and it is expressed in mol/L.

Equations 3−6 correspond to a typical experimental situation in which the catalyst is immobilized on a membrane, whereas the activator is in the solution and it can diffuse (compare refs 7 and 20). Therefore, we assume free boundary conditions between the active and passive areas.

In our numerical calculations for the B−Z system we use the same values of parameters as considered in refs 13, 14, and 21: $A = 0.02$ M; $B = 0.2$ M; $C = 0.001$ M; $k_1 = 100\ \mathrm{M^{-2}}/sec$; $k_4 = 1.7 \times 10^4\ \mathrm{M^{-2}/sec}$; $k_5 = 10^7\ \mathrm{M^{-2}/sec}$; $k_7 = 15\ \mathrm{M^{-2}/sec}$; $K_8 = 2 \times 10^{-5}$ M/sec; $k_{13} = 10^{-6}\ \mathrm{s^{-1}}$; $q = 0.5$. The corresponding values of scaled parameters α, β, ϵ, and μ are $0.017h_0^{-2}$, $0.0017h_0^{-1}$, 0.1176, and 0.00051, respectively. For these values of parameters the system becomes excitable if $h_0 < 0.9899$.[21]

Equations 3−6 are written in the dimensionless units of time τ and distance ρ. The relationships between them and the real time t and distance r are the following:

$$t = \frac{k_4 C}{k_1^{\,2} A^2 h_0} \tau \tag{13}$$

$$r = \sqrt{\frac{k_4 C}{h_0}} \frac{1}{k_1 A} \sqrt{D_{\mathrm{x}}}\, \rho \tag{14}$$

where D_x is the diffusion constant of the activator x. The expressions (13) and (14) lead to the following relationship between real υ and dimensionless ν velocities of a pulse:

$$\upsilon = k_1 A \sqrt{\frac{h_0}{k_4 C}} \sqrt{D_X}\, \nu \tag{15}$$

The constant which transforms τ into t is immediately fixed when the values of A, B, C, and h_0 and the rate constants $k_{\pm i}$ are defined. For the parameters chosen and assuming $h_0 = 0.5$, it reads

$$t\ (\mathrm{s}) = 8.5\tau \tag{16}$$

Similar relationships for distance and velocity depend also on the values of the diffusion constant:

$$r\ (\mathrm{cm}) = 2.915\sqrt{D_X/(\mathrm{cm^2/s})}\Delta\rho \tag{17}$$

$$\upsilon\ (\mathrm{cm/min}) = 20.58\sqrt{D_X/(\mathrm{cm^2/s})}\nu \tag{18}$$

However, the diffusion constant strongly depends on the medium the reactions proceed in. In the aqueous solution it is of the order of $10^{-5}\ \mathrm{cm^2/s}$,[7,13,17,19,21] whereas for a reaction in a gel it may be reduced by 2 orders of magnitude.[7,22] To make our results more general, we present all distances and velocities in the double form: dimensionless and as the function of the ratio of diffusion constants D_X/D_{X_0}, where the value of D_{X_0} corresponds to a particular choice of the diffusion constant: $D_{X_0} = 1 \times 10^{-5}\ \mathrm{cm^2/s}$.[13,21] The second number allows one to see more clearly the real spatial and temporal scale of the considered process.

The system of partial differential eqs 3−6 has been solved numerically using the explicit Euler technique. The constant time step $d\tau = 0.001$ is used. The pulses are initialized at the boundaries by increasing the concentration of x to 0.1. Our experience with the cross junction for the FitzHugh−Nagumo model says that the switching properties of the system come as the consequence of the strong dependence of the penetration depth on the angle of incidence when a chemical pulse propagating on an active semiplane “hits” the boundary of another (passive) semiplane. For the FitzHugh−Nagumo model the penetration depth for a pulse propagating parallel to the line of junction is by 6% smaller than the penetration depth for a pulse propagating perpendicularly d_c.[4] It means that a passive layer of a width d ($0.94d_c < d < d_c$) is transparent for a pulse propagating perpendicularly but impenetrable for a pulse propagating parallel to it (for convenience, let us call them a “perpendicular” and “parallel pulse”, respectively).

Studying the B−Z system, we have first considered $h_0 = 0.97$ and found that the penetration depths for pulses traveling perpendicularly or parallel to the line of junction of active and passive fields are almost the same, as they differ by less than 0.05%. Therefore it seems to be very difficult to make a passive stripe impenetrable for a “parallel pulse” and penetrable for a “perpendicular” one in the laboratory, even if the lithographic methods for the introduction of catalyst are used.[23,24] Plotting the isoclines of eqs 3 and 4 (without the diffusion term), one can notice that decrement of h_0 stabilizes the stationary solution of eqs 3 and 4. This results in a faster relaxation of the active medium and remarkably increases the asymmetry in the penetration depth. From the chemical point of view decreased h_0 corresponds to lower concentration of H^+ in the system. The further results have been obtained for $h_0 = 0.5$. In this case the stationary concentrations of x and z in the active area are

$$x_{\mathrm{sa}} = 7.283 \times 10^{-4} \tag{19}$$

$$z_{sa} = 1.060 \times 10^{-2} \tag{20}$$

(which is the stationary solution of eqs 3 and 4) and the stationary concentrations in the passive area (the stationary solution of eqs 5 and 6) are given by

$$x_{sp} = 5.010 \times 10^{-4} \tag{21}$$

$$z_{sp} \equiv 0 \tag{22}$$

For $h_0 = 0.5$ the penetration depth for a "parallel pulse" is about 1% smaller than for a "perpendicular pulse". Creating a stripe of passive field with higher than 1% accuracy in its width is still a hard but not an impossible task from the experimental point of view.

What makes the Rovinsky−Zhabotinsky model more sensitive to the width of a passive barrier than the FitzHugh−Nagumo one? We believe that the essential difference comes from the reactions in the passive area. The observations of pulses crossing a barrier have demonstrated that in the FitzHugh−Nagumo model the values of concentration of activator (u) within the barrier are similar to those in a propagating pulse. Contrary, the reactions appearing in the Rovinsky−Zhabotinsky model (eq 5) reduce the concentration of x by 2 orders of magnitude with respect to its amplitude in the active area. The reactions make the penetration depth far less sensitive to the direction of incident pulses.

To estimate penetration depths let us consider a plane filled with a catalyst (i.e. in an active state) divided by a stripe of a passive region. Initially both active and passive regions are in their stationary states. Next, we initiate a plane pulse of excitation. Performing a set of numerical experiments for different widths of the passive stripe, we have found it is transparent for a "perpendicular pulse" but impenetrable for a "parallel" one if the width of the stripe is within the interval [3.287, 3.318) in the dimensionless units. In the real scale it is equal to [$0.03029\sqrt{D_X/D_{X_0}}$ cm, $0.03059\sqrt{D_X/D_{X_0}}$ cm). According to our calculations the passive stripes narrower than 3.287 ($0.03029\sqrt{D_X/D_{X_0}}$ cm) are penetrable for any pulse of excitation, independently of its direction, whereas the stripes wider than 3.318 ($0.03059\sqrt{D_X/D_{X_0}}$ cm) are always impenetrable. Experimental studies on penetration of a passive stripe may bring important information on the applicability of eqs 3−6.

Next we have considered the geometry presented in Figure 1. In the majority of calculations the square is covered with a grid of 320 × 320 points. At the beginning the concentrations of x and z in both active and passive areas correspond to their stationary states x_{sa}, z_{sa} and x_{sp}, z_{sp}, respectively. The boundary conditions between the excitable and diffusion fields are free. We use no flux boundary conditions on the lower and on the left-hand side border of the system. On the other hand, we fix the values of x and z as equal to the corresponding stationary states (x_{sa}, z_{sa}, and x_{sp}, z_{sp}, respectively) at the upper and the right-hand side border. This way the pulses that arrive there may freely "leak out" of the system (they do not accumulate in the neighborhood of the border) and we avoid any influence of the system's boundary on the time evolution. The pulses in the signal channels 4−5−6 and 8−5−2 (see Figure 1) are generated by increasing x to the value 0.1 at the boundaries of areas 4 and 8. We have considered the passive stripes which are 3.291 ($0.03034\sqrt{D_X/D_{X_0}}$ cm) wide. From the calculations we have found the minimum width of the signal channels. For the selected width of the passive stripes the pulse initiated for example in area 8 always arrives to the central field 5. However, if the central field is too small then the amplitude of the activator is not high enough to excite the opposite area 2. We have found that the minimum inner width of the signal channel for which pulses can propagate through the junction is about 10.526 ($0.097029\sqrt{D_X/D_{X_0}}$ cm).

Knowing the width of a semitransparent passive barrier and the width of an active channel, we can build a cross junction of the excitable B−Z system which should work similarly to that for FitzHugh−Nagumo dynamics.[8] The pulses initiated in the horizontal channel (in area 4 in Figure 1) should be able to get through the junction (area 5 in Figure 1) and arrive at the other side of the device (area 6 in Figure 1) without escaping from the channel (to areas 1−3 and 7−9 in Figure 1) and due to the symmetry of the device the pulses in the vertical channel should behave in the same way. Now let us consider the interaction between pulses coming from perpendicular directions. At the beginning the system is in its stationary state. In calculations we consider two sizes of the square the junction is built on: 198.13 × 198.13 and 263.3 × 263.3 (corresponding to $1.8264\sqrt{D_X/D_{X_0}}$ cm and $2.427\sqrt{D_X/D_{X_0}}$ cm), for which we use square lattices of 240 × 240 or 320 × 320 points, respectively. Thus, the space step in all these simulations $d\rho = 0.82$ remains constant. Two channels with the width of 66.648 ($0.61436\sqrt{D_X/D_{X_0}}$ cm) or 132.473 ($1.22114\sqrt{D_X/D_{X_0}}$ cm) for smaller and larger system respectively are placed symmetrically on the square. In all the computer experiments the width of the diffusion stripes is 3.291 ($0.03034\sqrt{D_X/D_{X_0}}$ cm). The results obtained for different grids are consistent. The first pulse is initiated on the left-hand side border of the area 4 in Figure 1. After a time $\Delta\tau$ another pulse is initiated on the lower border of the area 8. Because the distance from both borders to the junction is the same, the time difference between the arrival of the first and the second pulse at the junction is also $\Delta\tau$.

We observe that if the second pulse arrives at the central field earlier than $\Delta\tau_{min} = 107$ (910 s) after the first one, it is stopped at the central field. On the other hand if $\Delta\tau > \Delta\tau_{max} = 115$ (978 s), both pulses follow their signal paths without interaction.

Although we are able to build a coincidence detector on the basis of the cross junction of excitable B−Z systems with the dynamics given by the Rovinsky−Zhabotinsky model, the other interesting features of the junction, described in ref 8, do not occur in the model used here. In particular, we do not observe the "AND" logical gate behavior, when two pulses coincide, producing an output pulse between the channels (in areas 7 or 9 in Figure 1), or the "chemical switch", when the second pulse changes the direction of propagation and follows the first one.[8]

To see more clearly why the "chemical switch" does not work for the B−Z system, we have performed calculations for the unsymmetrical junction presented in Figure 3. Here we use a 263.3 × 263.3 ($2.427\sqrt{D_X/D_{X_0}}$ cm) square, covered with the grid of 320 × 320 points. The width of the stripes of the diffusion field is $w = 3.291$ ($0.03034\sqrt{D_X/D_{X_0}}$ cm). The first pulse is initiated in the horizontal channel (area 4 in Figure 1). The channel is located at the distance $d_{lower} = 56.363$ ($0.51956\sqrt{D_X/D_{X_0}}$ cm) from the lower boundary; its width is $d_{horiz} = 99.560$ ($0.91775\sqrt{D_X/D_{X_0}}$ cm). After the time $\Delta\tau = 109.0$ (927 s) another pulse is initiated in the vertical channel (area 8 in Figure 1). This channel is located at the distance $d_{left} = 56.363$ ($0.51956\sqrt{D_X/D_{X_0}}$ cm) from the left-hand side boundary; its width is $d_{vert} = 152.220$ ($1.40317\sqrt{D_X/D_{X_0}}$ cm). We see that when the second pulse gets to the central area of the junction, it propagates in both vertical and horizontal directions. The propagation to the right

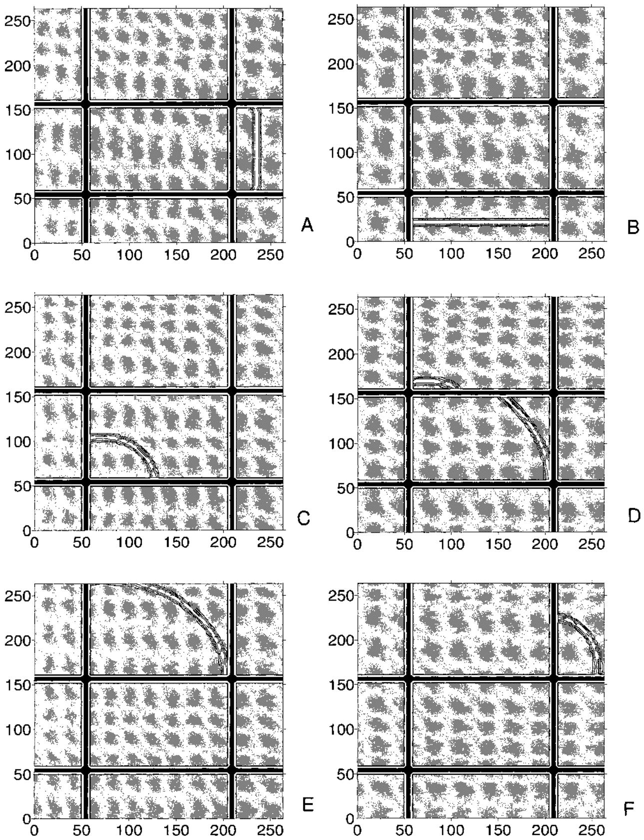

Figure 3. Two pulses in an unsymmetrical cross junction of systems with Rovinsky−Zhabotinsky dynamics. Figures show the concentration of activator for a few selected moments in the case the second pulse of excitation arrives $\Delta\tau = 109$ after the first one. The lighter areas correspond to higher concentration of x. (A) $\tau = 54$. The first pulse passes through the horizontal channel. (B) $\tau = 114$. The second pulse approaches in the vertical channel. (C) $\tau = 134$. The second pulse propagates asymmetrically in the central area. (D) $\tau = 150$. Although the geometrical condition is fulfilled, the pulse cannot pass into area 6, while it gets into area 2. (E) $\tau = 170$. Asymmetrical propagation of the second pulse occurs in area 2. (F) $\tau = 184$. The pulse gets into area 3.

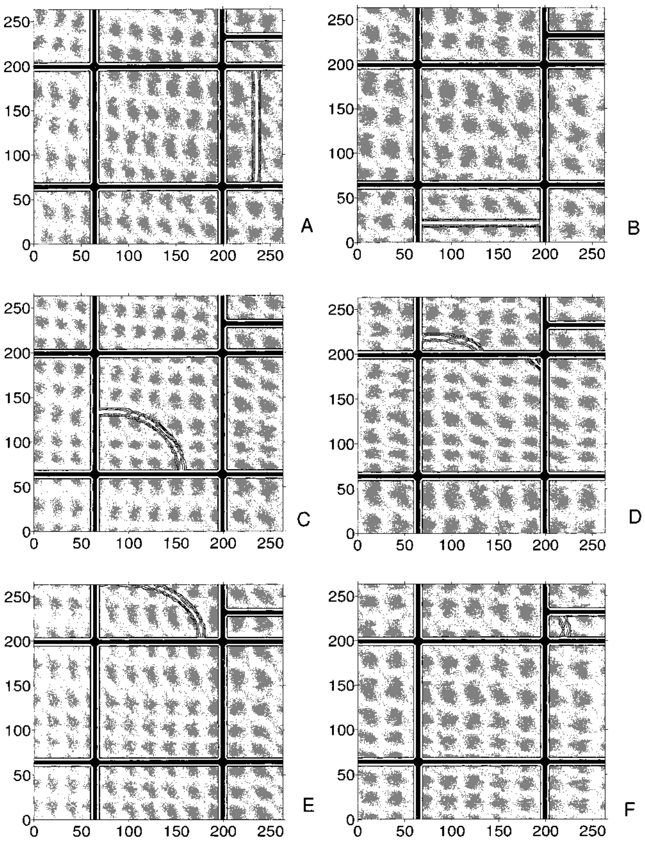

Figure 4. Two pulses in a symmetrical cross junction of systems with Rovinsky−Zhabotinsky dynamics with an additional channel. Figures show concentration of activator for a few selected moments in the case the second pulse of excitation arrives $\Delta\tau = 109$ after the first one. The lighter areas correspond to higher concentration of x. (A) $\tau = 54$. The first pulse passes through the horizontal channel. (B) $\tau = 114$. The second pulse approaches in the vertical channel. (C) $\tau = 140$. The second pulse propagates asymmetrically in the central area. (D) $\tau = 160$. The pulse is stopped on the right-hand side boundary of the vertical channel. (E) $\tau = 170$. Asymmetrical propagation of the second pulse occurs in area 2. (F) $\tau = 182$. The pulse gets into area 3 (as in Figure 3F) but also generates a pulse in the extra channel.

fails, while the propagation upward continues, and what is very important, the pulse is able to pass from its own channel (area 2 in Figure 1) to the upper right-hand side part of the system (area 3 in Figure 1). Comparison of Figures 3D,E shows that the pulses trying to get from region 5 to 6 and from region 2 to 3 (in Figure 1) "attack" the stripe of the diffusion field both at the same angle, so the geometrical factor is not the reason for the propagation failure. The failure occurs apparently because the active medium in area 6 is still not relaxed after the first pulse. We have performed a set of simulations for a set of smaller time shifts $\Delta\tau$ (until the second signal is not able to enter the junction at all for $\Delta\tau = \Delta\tau_{\min} = 107$ (910 s)) as well as for the larger ones (until the second signal propagates through the junction and does not "feel" the influence of the first signal at all for $\Delta\tau = \Delta\tau_{\max} = 115$ (978 s)) and have never found the second signal turning right from area 5 to 6. So, we have not found the "chemical switch" behavior in the Rovinsky−Zhabotinsky model, even though the geometry of the system favors it!

The difference with respect to the FitzHugh−Nagumo model may be explained as follows: in the Rovinsky−Zhabotinsky model the distance at which inhibitor (z) relaxes is by 1 order of magnitude larger than the one for activator (x), whereas for FitzHugh−Nagumo both u and v relax at the same spatial scale.

Looking at Figures 3E,F, we can see that the simplest idea on how to turn the second pulse right is to direct the pulse excited in the upper right-hand side corner of the system (area 3 in Figure 1) into an additional channel. This has been done in the computer experiment illustrated in Figure 4. The sizes of the square, grid size, width of the diffusion stripes, and the time shift between the signals are the same as in Figure 3. The main channels have identical width of $d_{\text{channel}} = 132.473$ ($1.22114\sqrt{D_X/D_{X_0}}$ cm) and they are placed symmetrically in the middle of the square (at the distance $d = 66.236$ ($0.61057\sqrt{D_X/D_{X_0}}$ cm) from each border). An extra channel of the diameter $d_{\text{extra}} = 33.735$ ($0.31097\sqrt{D_X/D_{X_0}}$ cm) is located in the upper right-hand side corner of the system. In Figure 4F one can see that the pulse is in fact excited in that extra channel. Our results suggest that this type of behavior can be observed (at least) for $\Delta\tau \in [108,111]$ (918, 944 s).

Another way of building a "chemical switch" is to speed up the relaxation of the active chemical medium in the area 6 behind the first pulse. One can do it easily by increasing the diffusion coefficient in the region 6. Now a pulse propagates faster, and the recovery time of the medium is shorter. The idea is demonstrated by results of another computer experiment presented in Figure 5. The geometry is the same as in Figure 4, except there is no the extra channel. Instead, the diffusion

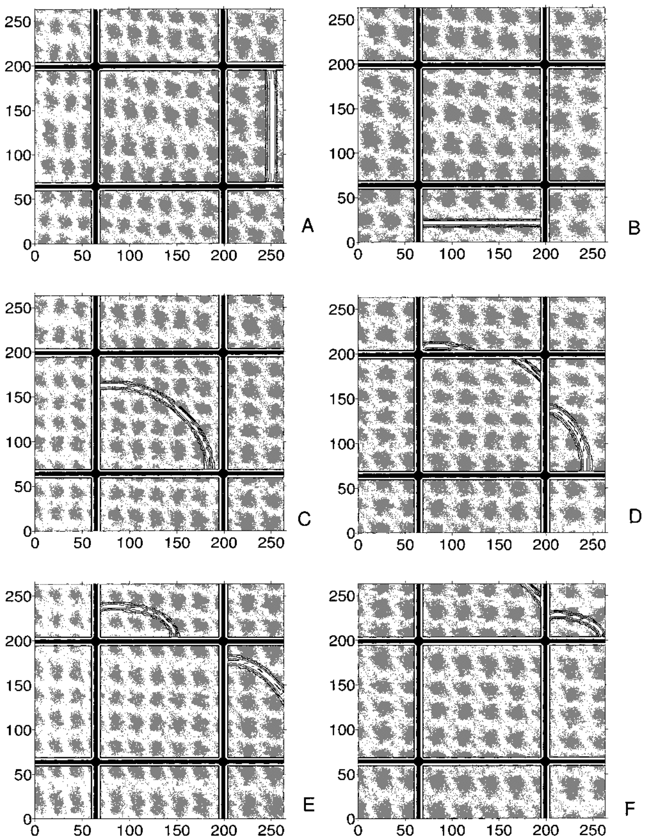

Figure 5. Two pulses in an unsymmetrical cross junction of systems with Rovinsky−Zhabotinsky dynamics, in the case of faster diffusion in the area 6. Figures show concentration of activator for a few selected moments in the case the second pulse of excitation arrives $\Delta\tau = 109$ after the first one. The lighter areas correspond to higher concentration of x. (A) $\tau = 54$. The first pulse passes through the horizontal channel. (B) $\tau = 114$. The second pulse approaches in the vertical channel. (C) $\tau = 146$. The second pulse propagates asymmetrically in the central area. (D) $\tau = 158$. The pulse is doubled: it turns right into area 6 and follows its original path (area 2). (E) $\tau = 164$. Asymmetrical propagation of the second pulse occurs in areas 2 and 6. (F) $\tau = 176$. The pulse from area 6 excites a pulse in the area 3.

coefficient of the activator is doubled in the area 6, if compared to the rest of the system. The first pulse travels in the horizontal channel (areas 4−6 in Figure 1) and speeds up remarkably after crossing the junction (in area 6 in Figure 1). After $\Delta\tau = 109.0$ (927 s) a pulse in the vertical channel is initiated. This second pulse gets through the junction (within its own channel, area 2 in Figure 1), but also, as required, it follows the first pulse. As in the previous simulation (Figure 4) this behavior can be observed (at least) for $\Delta\tau \in [108,111]$ (918, 944 s).

The typical velocity of the pulse in our system is about 4.128 ($0.2686\sqrt{D_X/D_{X_0}}$ cm/min), which is a reasonable value for a chemical wave in the B−Z reaction.

Conclusions

In this paper we have demonstrated that the properties of a cross junction of active fields with FitzHugh−Nagumo dynamics studied in our previous paper[8] can be realized in a junction of excitable systems with Belousov−Zhabotinsky reaction. These properties include coincidence detection (the pulses coming within times shorter than a characteristic one are stopped) and switching the direction a chemical pulse propagates.

We have found that to construct a working cross junction on the basis of the Belousov−Zhabotinsky system one needs to create passive stripes with a very high accuracy. If the diffusion constant of the activator corresponds to the value characteristic for an aqueous system (D_0), then the stripe without catalyst should be 0.3034 mm wide with only 1% of tolerance. We think that so high precision can be achieved with the newly developed lithographic technique of introducing catalyst on the surface[23,24]

The most interesting feature of a cross junction is its ability to switch the direction of an incoming signal. We have discovered such effect for a symmetric cross junction (the perpendicular signal paths are of equal width) and FitzHugh−Nagumo dynamics. Nevertheless, we are unable to find a similar effect for the B−Z system, which seems to be connected to its slower relaxation. We have found that a switch of a chemical signal can be constructed if a cross junction of excitable B−Z systems is not symmetric. Two working schemes, in which the asymmetry is related to the diffusion coefficient or to the existence of another output channel, have been studied.

Our numerical "experiments" have shown that the width of signal channels does not have significant influence on the behavior of the cross junction (if only the channels are wider than the minimum 0.9703 mm). The system for which the signal paths are three times wider than those shown in Figures 4 and 5 have been investigated (thus, the signal channels are 3.66 cm wide). It has been found that for this system the pulses which arrive earlier than $\Delta\tau = 100$ after the first one are stopped. Such result may be expected as the "transparency" of the central field is related to the time the system spends in the refractory regime, which hardly changes with size. On the other hand, the interval of times for which the system works as a signal switch becomes slightly longer for the larger system. This is related to the direction of propagation of the second pulse in the central area. We have observed that for three times wider signal channels (3.66 cm) the junction works as shown in Figure 3, even if the second pulse arrives $\Delta\tau = 120$ after the first one.

We believe that the suggested devices based on the cross junction of active fields extend a class of chemical systems, which process information and may be used as elements of more complex structures.

Last but not least, we mention that in the case of the Belousov−Zhabotinsky reaction such properties as the penetration depth strongly depend on the properties of the model. Therefore the comparison between calculations and carefully prepared experiments for a junction of passive and active areas may be a good verification of the model and the values of parameters used.

Supporting Information Available: The detailed step by step derivation of eqs 3−6 from the reaction scheme. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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