

# Information Transmission in a Diffusion-Coupled Oscillatory Chemical System

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An experiment on signal transmission in a chemical system involving the catalytic oxidation of malonic acid by bromate in an acidic medium is reported in this article.

Most chemical reactions proceed monotonically towards thermodynamic equilibrium, sometimes with the formation of intermediates which later disappear. But there are reactions in which intermediates and products appear periodically, such as the inorganic oscillating system described by Bray<sup>1</sup> and the oscillating advancement in a reaction system consisting of inorganic and organic compounds described by Belousov<sup>2</sup>. Also, oscillatory variations of intermediate compounds have been detected in biochemical systems such as the glycolytic pathway or the oxidative processes in mitochondria<sup>3</sup>. All these reactions have been observed under conditions far from thermodynamic equilibrium.

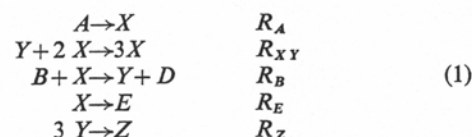
Synchronization of the phase of oscillations in different spatial locations is closely related to periodic time courses of chemical reactions. In suitable conditions, this leads to a spatial distribution of some components. Zhabotinsky<sup>4</sup> has described a chemical system similar to the one of Belousov<sup>2</sup> which displays such phenomena. The experiments, performed in long tubes, revealed a spatial pattern moving along the tube. Later, such experiments were improved and extended<sup>5,6</sup> demonstrating moving spiral, ring-shaped and more complex patterns. These patterns resemble structures observed during aggregation in a mutant of *Dictyostelium discoideum*<sup>7</sup> and may be related to those encountered in nerve cells. These examples differ from non-biological ones in that the spatial distribution of the oscillatory system carries information; indeed, in the case of aggregation, it defines the direction of movement.

Because of the complexity of equation systems describing oscillatory and spatial effects we deal only with some simplified mechanisms. We know that quasi-stable singularities of any dimension may lead to a new class of states; thus, movement in a limit cycle results in an oscillatory reaction advancement and coupled with diffusion can generate spatial effects. Such effects occur in special conditions of stability or instability, far from thermodynamic equilibrium. The combination of oscillatory and spatial effects and a description of the mathematical treatment of a localized space-time dependent structure and space-time responses under specified initial conditions are described in refs 8 and 9.

Can diffusion-coupled oscillatory chemical systems be used to transmit information over a longer distance? Here we use the bromate-malonic acid system to demonstrate signal transmission. Because the mechanism of the system is not known in detail, we chose a chemical reaction scheme similar to that of ref. 10 as a model.

## Elementary Chemical System

Lefever<sup>11</sup> described a simple chemical model system which has the essential properties of an oscillatory non-equilibrium state, that is, limit cycle behaviour. Analysis of the kinetic laws of this system demonstrated instability and periodicities in time and space as well as localized structures<sup>8</sup>. If one more trimolecular reaction ( $R_Z$ ) is added, sequence (1) is obtained:



The corresponding network (Fig. 1) is derived from the chemical reaction scheme of ref. 12 (see also refs 13, 14). Neglecting all reverse reactions, setting all forward rate constants to unity and  $A=1$ ,  $B=5$  the system moves on a limit cycle. The time dependence of some variables in extreme non-equilibrium conditions is illustrated in Fig. 1.

The oscillatory behaviour of this system resembles that of a relaxation oscillator<sup>15</sup>. A concentration (charge) is accumulated

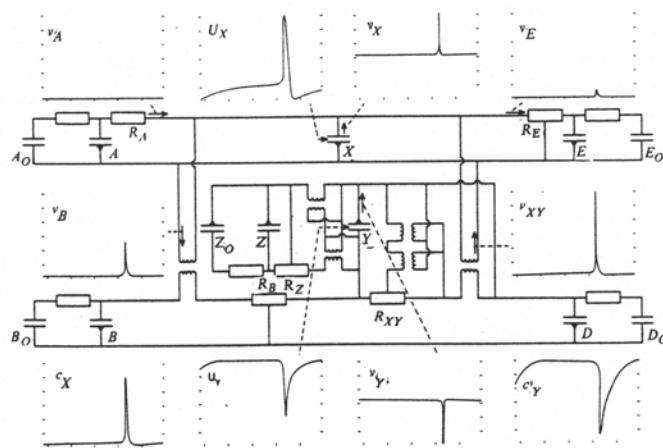
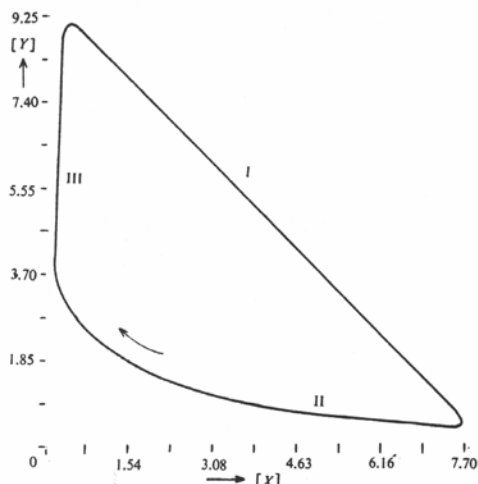


Fig. 1 Network of chemical reaction system (1):  $A$ ,  $B$ ,  $D$ ,  $E$ ,  $X$ ,  $Y$  and  $Z$  are chemical compounds corresponding to energy storing capacitors.  $A_0$ ,  $B_0$ ,  $D_0$ ,  $E_0$  and  $Z_0$  are chemical compounds serving as reservoirs to maintain constant concentrations of  $A$ ,  $B$ ,  $D$ ,  $E$  and  $Z$ . The oscillation proceeds by charging capacitor  $Y$  through  $R_B$  up to a threshold value against discharge through  $R_Z$ . Then reaction  $R_{XY}$  fires and discharges the capacitor  $Y$ .  $v$  is the rate of reaction.  $c_X$  and  $c_Y$  designate the variations in the concentration of  $X$  and  $Y$ .  $U_X$  and  $U_Y$  are the normalized chemical potentials. The fulltime scale is 52 units. The scaling unit starting from zero for  $v_A$ ,  $v_B$ ,  $v_D$  and  $v_{XY}$  is 15.6; the scaling unit for  $v_X$  and  $v_Y$  is about 19.2. Most of the times  $v_X$  and  $v_Y$  are close to zero. The scaling unit for  $c_X$  and  $c_Y$  is 1.53 starting from zero. The scaling unit for  $U_X$  and  $U_Y$  is 0.64.



**Fig. 2** Limit cycle of the chemical reaction scheme in Fig. 1. The conditions are the same as for Fig. 1. The scaling of concentration of  $X$  and  $Y$  is dimensionless. The motion on the limit cycle is discussed in detail by Lavenda *et al.*<sup>10</sup> for a scheme comprising the reactions  $R_A$  through  $R_E$ . In part I the autocatalytic step  $R_{XY}$  determines the transformation of  $Y$  into  $X$ . In part II  $X$  disappears by the steps  $R_E$  and  $R_B$  while  $Y$  remains small. In part III,  $X$  remains small while  $Y$  is accumulated by the step  $R_B$ . The additional step  $R_Z$  contributes to the movement only at high concentrations of  $Y$ , at the end of part III. Here most of the  $Y$  produced by the step  $R_B$  is consumed by  $R_Z$  resulting in a very slow approach to the critical concentration, which activates the autocatalytic step of part I. This analysis clearly demonstrates that in different portions of the limit cycle different chemical processes determine the motion of the system.

up to its threshold value and subsequently the capacitor ( $Y$  in Fig. 1) is discharged and the process starts anew.

The triangular form of the limit cycle of the essential components ( $X$  and  $Y$ ) (Fig. 2) indicates three different phases of the limit cycle.

To allow for diffusion processes the network must be extended by an additional resistive element describing the linear relation between the diffusion flux ( $I_D$ ) and its concentration gradient:

$$I_D = D \Delta c / \Delta x = D c^* (e^{U_{out}} - e^{U_{in}}) / \Delta x \quad (2)$$

$c^*$ ,  $c$  are reference concentration and concentration respectively;  $x$  a space coordinate;  $D$  the diffusion constant, and  $U$  the normalized chemical potential<sup>12</sup>.

The approximation for small concentration differences gives

$$I_D \approx D \bar{c} \Delta u / \Delta x \quad (3)$$

where  $\bar{c}$  is the geometric mean of the concentrations at the ports and  $\Delta u = U_{out} - U_{in}$ . This can be used to approximate a continuum adequately by a lumped network of resistive elements representing diffusion processes.

Assuming that only  $X$  diffuses we obtain for a space element the two-port network shown in Fig. 3 (upper schematic).

A chain of such one dimensional two-ports (Fig. 3, lower schematic) represents a transmission line, composed of symmetrical T-type two-ports. Because any element of the two-port is passive the whole two-port is passive. In the limit of a great number of infinitesimal lumped elements the behaviour of the line approximates that of a one dimensional continuum<sup>14</sup>.

## Analysis of Transmission Properties

To analyse properties of the transmission line its differential equation system obtained from rate processes of sequence (1) and the diffusion coupling between the line elements must be considered

$$\frac{dX_i}{dt} = A + X_i^2 \cdot Y_i - (B+1)X_i + q_x(X_{i-1} + X_{i+1} - 2X_i) \quad (4a)$$

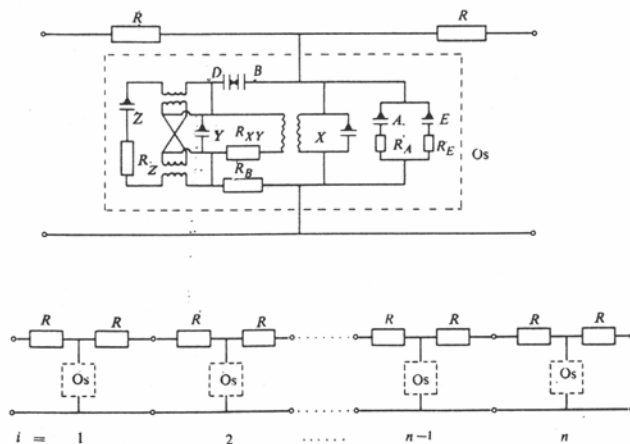
$$\frac{dY_i}{dt} = B \cdot X_i - Y_i^3 - X_i^2 \cdot Y_i \quad (4b)$$

where  $q_x = D_x / \Delta x$ ;  $D_x$  is the diffusion coefficient of  $X$  and  $\Delta x$  the length of the line represented by this element.  $i$  denotes the number of the oscillatory elements in the chain (Fig. 3, lower schematic). At  $i=1$  and  $i=n$  the concentrations  $X_0 - X_1$  and  $X_n - X_{n+1}$  are zero. The system of difference and differential equations<sup>4</sup> is solved by Hamming's modified predictor-corrector method.

Without diffusion each element moves independently on a limit cycle. Because the outflow/inflow of compounds from the neighbouring element can retard/enhance the motion on the limit cycle, the diffusion helps to synchronize neighbouring elements. But this happens only if the system is sensitive to an addition or subtraction of the compound.

There may be parts of the limit cycle where the motion is nearly independent of the state of the neighbouring elements and other parts where the motion is strongly dependent on them. Further, during the sensitive part the diffusion leads to an equilibration of the phase differences between neighbouring cycles.

In system (1) the sensitive part of the limit cycle is exemplified at the end of portion III (Fig. 2). If, in this portion of the limit cycle, compound  $X$  is added to an oscillatory element the autocatalytic process (portion I) starts considerably earlier than otherwise. All elements which show a high  $Y$  and a low  $X$  concentration will immediately start their autocatalytic process when the neighbouring element has a sufficiently higher concentration in  $X$ ; as soon as an element moves into the sensitive part of its limit cycle the interaction with its neighbour determines its future motion. In a chain of oscillatory elements all having high  $Y$  and low  $X$  concentration, the element which first starts its autocatalytic process will force its neighbour to follow. If the autocatalytic process of the first element is triggered externally, a triggered pulse moves along the chain.



**Fig. 3** The upper network is a symmetrical T-type four terminal network comprising the two resistors  $R$  originating from the diffusion process and the cross linking network enclosed in the dashed box,  $O_s$ . The  $O_s$  network is a rearranged drawing of the network given in Fig. 1 and the diffusive resistors  $R$  are added. Finally, all connexions not carrying a net current are omitted and the pools are eliminated. In the lower network a series of these two-ports is arranged in a chain in order to form a transmission line, composed of equal oscillatory units.

To achieve an optimized transmission the concentration of  $Y$  of system (1) should be maintained for a long time in the sensitive phase below its critical value. Then the pulse might travel a long distance before it reaches the limit where it interferes with the natural frequency of the oscillatory elements (step  $R_Z$  of system (1)).

A computation of a transmission line is represented in Fig. 4. Three trigger pulses at different time intervals are given to the first oscillatory element in the line. The signals run along the line almost undistorted and with nearly constant velocity.

## Experimental Signal Propagation

Under suitable conditions the catalytic oxidation of malonic acid by bromate shows a wave-like distribution of the catalyst in space and time<sup>4</sup>. Also, the oscillatory oxidation can be influenced by ultraviolet flashes<sup>16</sup>. These phenomena may be combined to demonstrate the initialization of a propagating wave by ultraviolet radiation.

A typical experiment is carried out in a Petri dish onto which an ultraviolet beam is directed. The beam of a 450 W xenon-arc filtered for ultraviolet is focused to a diameter of about 0.4 cm on the solution layer, approximately 2 mm thick. After the solution is phase balanced by shaking, the "light" pulse is switched on in the blue phase of the oscillation for 2 to 30 s.

A wave propagates from the centre of the initiation with nearly constant velocity until after about 1 to 2 cm the wave disappears in the oscillation of the bulk solution (Fig. 5). During the next period, at the spot illuminated before, the solution turns blue before the bulk solution turns blue and again a wave starts from this position, disappearing in the oscillation of the bulk solution (see Fig. 5d).

## Significance of the Experiment

Because no adequate chemical reaction scheme for the malonic acid-bromate or other oscillatory chemical systems is available, a comparison of experimental and theoretical results can only be qualitative.

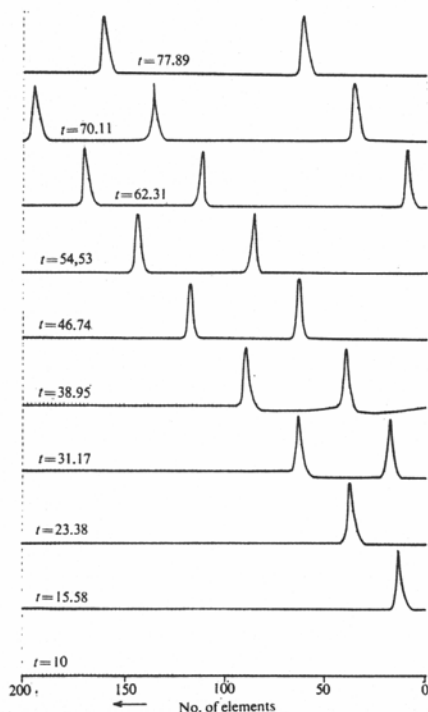


Fig. 4 Computer output of a transmission line demonstrating the propagation of pulses by which information is transferred. For 200 elements of the line the concentration of  $X$  is plotted at time  $t$ . The number of elements is plotted right to left. The curves are generated by sequence (1). The data for the oscillatory circuit are those of Fig. 1. The rate constant for step  $R_z$  is chosen  $8.992 \times 10^{-4}$  and the coupling constant of the diffusion  $q_x = 0.35$ . Here, the first element is triggered by a series of three pulses with distinct time intervals.

The common qualitative property in our theoretical system and the experimental system is the motion on a quasi-stable limit cycle. This cycle must have at least one portion that can be perturbed by a superimposed diffusional flow of chemical substances. Although a linear one-dimensional motion is computed, whereas the experiments show moving rings, the common feature of the initiation of a propagating wave remains.

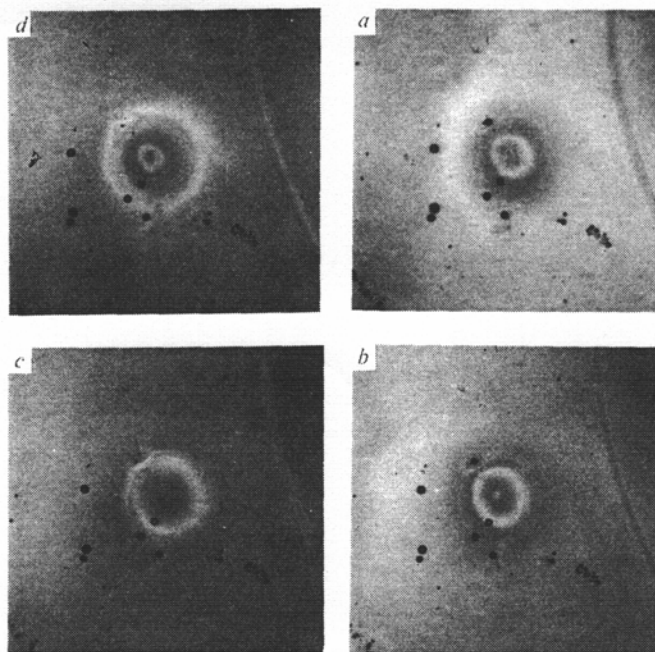


Fig. 5 Propagation of a signal in an oscillatory chemical reaction system. The initial concentrations of the solutions are

$[\text{KBrO}_3] = 0.35 \text{ M}$ ;  $[\text{H}_2\text{C}(\text{COOH})_2] = 1.2 \text{ M}$ ;  
 $[\text{Ce}(\text{SO}_4)_2] = 3.9 \times 10^{-3} \text{ M}$ ;  $[\text{Ferriin}] = 0.48 \times 10^{-3} \text{ M}$  in 3 N  $\text{H}_2\text{SO}_4$

About 15 min after initiation of the reaction by addition of the catalyst the ultraviolet pulse is given and shortly afterwards pictures are taken with an interval of 0.5 s. The sequence of the pictures shown is clockwise from (a) to (d). The white ring represents the blue outward moving wave, the spot in the centre was irradiated. Further explanations see text. In d, the following wave is already forming. Other conditions do not show both wave rings simultaneously, but the irradiated spot always turns blue ahead of the bulk solution to form a new wave centre.

Other types of triggering in the solution can be used as information input, because in the solution the initiation should be independent of the propagation.

A combination of two or more signals in a specified way may be considered as an operation on the information contained in the signals; such combinations may lead to a network made of "chemical wires".

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