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Autowave Processes in a Distributed Chemical System

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The autowave processes with a characteristic wavelength and oscillation period may arise under some initial conditions in a uniform active medium. The wavelength and period depend on the chemical and physical parameters of the system and are independent of the initial and boundary conditions and of the system linear size. The processes occur in a homogeneous solution in the course of an oscillating chemical reaction. Similar processes may play an important role in the phenomena of short-term memory, cardiac arrhythmia, morphogenesis and prebiological evolution.

Different types of structures are discussed, and experimental data and mathematical models are presented.

1. Introduction

This paper deals with distributed systems, in which every point of space is self-oscillating or potentially self-oscillating and there is diffusion type coupling between the points. The class of such systems consists of distributed concentration systems (chemical and ecological) and active non-linear RC-lines (in particular, biological membranes). In such systems stationary periodical wave processes may proceed and are accompanied by the appearance of spatial structures with characteristic dimensions, independent of boundary and initial conditions.

By analogy with auto-oscillations (self-oscillations) in point systems, the phenomena may be termed autowave processes (AWPs) as proposed by Professor R. V. Khokhlov. The AWPs and similar processes are believed to play an important role in the phenomena of short-term memory, cardiac arrhythmia, morphogenesis and prebiological evolution (Hebb, 1949; Moe, Rheinboldt & Abildskov, 1964; Turing, 1952; Krinsky, 1968; Prigogine & Nicolis, 1967, 1971; Goodwin & Cohen, 1969). AWPs are closely related to so-called "dissipative structures", which have been studied theoretically by Prigogine and his school mainly from a thermodynamic point of view (Prigogine & Nicolis, 1967, 1971). We have used the kinetic approach rather than thermodynamics which would reveal the loss of stability only, while AWPs may also occur when a spatially uniform steady state is stable (according to Liapounov).

We have experimentally discovered AWPs in a distributed chemical system in which an oscillating reaction of oxidation of malonic acid (or related compounds) by bromate occurred (Zaikin & Zhabotinsky, 1970; Zhabotinsky & Zaikin, 1971*a*).

2. Experimental Results and Models

(A) POINT SYSTEM—SYSTEM OF IDEAL MIXING

(Zaikin & Zhabotinsky, 1970; Zhabotinsky, 1964;
Vavilin, Zhabotinsky & Zaikin, 1971)

The system with Fe $(\text{phen})_3$ (designated below as Fe) as a catalyst and bromomalonic acid (BMA) as a reductant was commonly used in studies of spatial effects. The system was designated as BFB (bromate-ferroin-bromomalonic acid).

In most cases relaxation self-oscillations took place in the system with oscillation period (T) which was clearly divided into two parts: T_1, the phase of the Fe^{3+} concentration increase and T_2, the phase of the Fe^{3+} concentration drop. Correspondingly (by a simplified scheme) the reaction had two stages. During stage 1 ferroin was oxidized in the following reaction:

$$Fe^{2+} \xrightarrow{HBrO_3} Fe^{3+}. \qquad (1$$

In stage 2 reduction took place:

$$Fe^{3+} \xrightarrow{BMA} Fe^{2+}. \qquad (2)$$

Reaction (1) is an autocatalytic one in which the autocatalyst is not ferriin but an intermediate of bromate reduction. Products of bromate reduction, having been formed by reaction (1), brominated BMA. Bromide ion was formed as a result of decomposition of bromoderivatives which was induced by ferriin oxidation of BMA. The oxidation of BMA by ferriin also produced Br^-. Bromide was a strong inhibitor of reaction (1).

An oscillatory cycle may be qualitatively described in the following way. Suppose, that there is some Fe^{3+} concentration in the system. Then Br^- being formed in the course of stage 2, interacts with active intermediates of reaction (1) and disappears from the system at a certain rate. If the bromide concentration is high enough, reaction (1) is retarded. When $[Fe^{3+}]$, diminished due to reaction (2), reaches a lower threshold, the Br^- concentration drops abruptly. Reaction (1) starts at a high rate and Fe^{3+} concentration increases. When $[Fe^{3+}]$ reaches an upper threshold, the Br^- concentration increases sharply stopping reaction (1). The cycle is then repeated.

The mathematical model of the reaction is analogous to that of the reaction with Ce as a catalyst (Zhabotinsky, Zaikin, Korzoohin, Kreitzer, 1971*a*,*b*). It represents the second-order system of differential equations:

$$\dot{u} = f(u, w),$$
$$\dot{w} = g(u, w). \tag{3}$$

If system (3) is a model of our oscillating reaction, u is the concentration of the autocatalyst of reaction (1), and $w = [\mathrm{Fe}^{3+}]$. In this case isoclinic lines of system (3), $f = 0$, $g = 0$ are qualitatively shown in Fig. 1, where only the relative positions of the lines are shown. Position I corresponds to self-oscillations, in positions II and III the steady state is stable and the system behaves like a monostable generator (start–stop multivibrator). The transition from case I to II and then to III may be obtained by decreasing the acidity or bromate concentration or by increasing the BMA concentration.

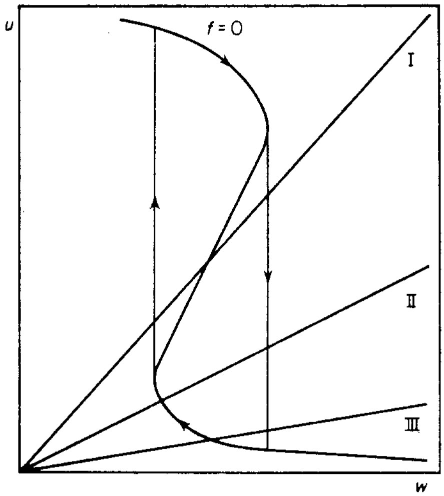

FIG. 1. Phase plane of system (3). I, II and III are the isoclines $g = 0$ corresponding to different regimes of the system. I, Self-oscillations (the limit cycle shown corresponds to relaxation self-oscillations); III, monostable; II, monostable in a point system (in a distributed system self-oscillation may occur). $f < 0$ to the right of the isocline $f = 0$, $f > 0$ to the left of it; $g > 0$ above the isocline $g = 0$, $g < 0$ below it.

(B) DISTRIBUTED SYSTEM

Experimental investigations were made in quasi-one-dimensional and quasi-two-dimensional systems, i.e. in the channel with cross-section 1 mm × 1 mm filled by reaction solution or in the layer of solution of about 1 mm deep.

A distributed system was described by the system of equations:

$$\frac{\partial u}{\partial t} = f(u, w) + D_u \Delta u$$

$$\frac{\partial w}{\partial t} = g(u, w) + D_w \Delta w. \qquad (4)$$

We considered the situations in which f and g were not explicit functions of the co-ordinates (spatial uniform system) and time, except for the specially mentioned cases (D = constant). (In the case of the RC-line, the diffusion coefficient D must be replaced by 1/RC.)

(i) *Single travelling wave*

The problem of propagation of single wave in a one-dimensional system is well studied. It includes propagation of flame, nerve impulse, etc. (Hodgkin, 1964; Frank-Kamenetsky, 1967). The basic result is the existence of the solution which depends on one co-ordinate only in the running co-ordinate system (self-modelling solution). The velocity of propagation is constant. The main condition for the existence of such solution is the presence of threshold, as in situations II and III in Fig. 1. The connection of the concept of the excitation threshold (for instance, in physiology) with the properties of the system like equations (3) has been discussed (e.g. Fitz-Hugh, 1961).

In the system BFB the propagation of a single wave was observed in state III (Fig. 1) under conditions: $NaBrO_3$ = 0·23 M, BMA = 0·16 M, $Fe(phen)_3$ = 0·003 M, H_2SO_4 = 0·26 M, T = 14°C. The wave velocity equalled approximately 0·01 cm/sec.

(ii) *Leading centre*

Relaxation self-oscillations with period T_0 occurred while stirring in the system BFB in case I (Fig. 1). In this instance leading centres (LCs) appeared in the distributed system where synphase oscillations with period T_0 (basic oscillations—BOs) took place. LCs were points in which oscillation period (T_{LC}) were shorter than T_0 (Zaikin & Zhabotinsky, 1970). Concentration waves propagate from LCs with a constant velocity. The waves occupied all the space step-by-step and oscillations with period T_{LC} occurred in every point of the space.

The wave velocity was constant, independent of T_{LC} and dependent on the reagent concentrations and temperature. The period of oscillations of every LC was constant in time. However, the periods of oscillations of different LCs varied more than twofold in one experiment. The cause of the variations was not known; it is possible that T_{LC} depends on the initial conditions.

Occasionally LCs rose at microheterogeneities and bubbles of CO_2. The LC, arising near the reactor edge, usually had T_{LC} significantly shorter than the mean T_{LC}. The wavelength (λ_{LC}) was determined by the expression

$$\lambda_{LC} = vT_{LC}.$$

We have studied the causes of the LC initiation (Zhabotinsky & Zaikin, 1971*b*). It has been shown that the mean number of leading centres per unit of the reactor area and the mean period of LC oscillations depend on the parameters of the system—concentrations of the oxidant and reducer and acidity. At the same time these values are practically independent of incidental contaminations and the material of which the reactor is made.

The experiments were performed using reagents extra purified from heterogeneous microcontaminations by repeated filtration. In other experiments chromatographic aluminium oxide powder was added into the system. In all cases the mean number of LCs and the mean T_{LC} were similar.

We have experimentally shown that local non-uniformity in the initial conditions may be a cause of LC initiation. If the autocatalyst in an overthreshold concentration is locally placed into an unexcited region, it is likely that, from this point, an oxidation wave will propagate (much like the flame propagation)—this is a trivial effect. An important fact is that at this point an LC can arise. The overthreshold concentration can also be caused by fluctuations.

The experiment was carried out in the following manner: from the front of the external wave of one of the LCs a small volume of the solution was transferred into some point in a wave-free region at the moment when this region was in a reduced state. At this point an LC appeared. The described procedure did not affect the system parameters, for nothing was brought into the system from the outside. It was proved that the procedure itself produced no LC, because the transfer of a portion of the solution from one point of an unexcited (reduced) region into another point of the same region gave no visible effect.

The LCs also appeared in a narrow region of the parameters, where the point system was stable (case II, Fig. 1). In this case BOs were absent in the system (Plate I).

In cases I and II (Fig. 1) the LC existed after its appearance until it was annihilated by a neighbouring LC with a shorter T_{LC}. There was a very narrow band separating regions II and III, where an LC existed during only 3 to 5 cycles after its appearance. Thus, locally stable LCs existed in regions I and II, and unstable LCs existed near the boundary between II and III.

The LC-problem may be divided into two parts from a theoretical point of view.

(1) *Wave propagation from LC.* In this case the LC by itself was considered only as a source of periodical influence. Within the scope of such a model it can be shown that the stationary regime has settled in the neighbourhood of an LC. The stationary regime zone gradually widened and gradually occupied all the reactor. The character of wave propagation within the stationary zone depends on a specific kind of the model. Interaction of waves propagating from different LCs was considered on the assumption of the constancy of the wave velocity (Zaikin & Zhabotinsky, 1970).

(2) *The problem of arising and self-sustaining of an LC.* LCs were observed experimentally in one- and two-dimensional systems. Registration of LC in a three-dimensional system was difficult. In this paper theoretical consideration was primarily made for a one-dimensional case.

It has been shown experimentally that:

(a) an LC arose in a uniform system under particular initial conditions;
(b) within a certain range of parameters, the disturbance exceeded some threshold value for an LC to arise;
(c) $T_{\mathrm{LC}} < T_0$;
(d) an LC existed both at the edge and in some inner point of the line. In the latter case the LC was a local centre of symmetry, where

$$\frac{\partial u}{\partial x} = \frac{\partial w}{\partial x} = 0. \tag{5}$$

Where an LC was situated at the edge of the line, condition (5) also took place and was due to impermeability of the reactor wall. Consequently, an LC is analogous to an antinode in a standing wave.

Difficulties of investigation of equations like equations (4) are well known. At present, we do not know any analytical procedure showing what kinds of $f(u, w)$ and $g(u, w)$ in system (4) are needed for an LC to arise. (Practically every kind of $f(u, w)$ and $g(u, w)$ can be realized in a chemical system. See Appendix.)

There are two approaches to the problem. *The first approach* is based on travelling waves which come from an LC. One can assume that the travelling waves create special conditions for self-oscillations at the point from which they come.

It seems evident that the time behaviour of the concentrations in a point X_0 from which waves are propagating differs from the behaviour in an ordinary point (in the zone of stationary waves or in that of synphase oscillations).

The last assumption has been supported by the model example in which point system behaviour is described by an explicit function of time and not by equations (3) (Zhabotinsky & Zaikin, 1971*b*):

$$\frac{\partial u}{\partial t} = q[\delta(x-vt)-\delta(x-vt-vT_1)]+D\frac{\partial^2 u}{\partial x^2}. \tag{6}$$

Since LCs with $T_{\mathrm{LC}} < T_0$ (including $T_0 = \infty$) have been experimentally observed one may conclude that the necessary condition for LC existence is $T_v < T_0$ (T_v is a period of self-oscillations in a stationary periodic wave travelling with constant velocity v). Consideration of travelling waves makes the analysis of models easier since it permits one to pass to the running coordinate system. Let us introduce a local time:

$$\tau = t \pm \frac{x}{v}. \tag{7}$$

Then equations (4) are transformed into

$$\frac{\mathrm{d}u}{\mathrm{d}\tau} = f(u,w) + \frac{D_u}{v^2}\frac{\mathrm{d}^2 u}{\mathrm{d}\tau^2},$$

$$\frac{\mathrm{d}w}{\mathrm{d}\tau} = g(u,w) + \frac{D_w}{v^2}\frac{\mathrm{d}^2 w}{\mathrm{d}\tau^2}. \tag{8}$$

Analysis of equations (8) is much easier than for equations (4). Suppose that for the existence of an LC in system (4) the oscillation period in system (8) must be shorter than in system (3). The approach was tested on a model with the following point system:

$$\dot{u} = (\kappa_1-\kappa_2 u+u^2w)(1-\kappa_2\kappa_3-2\kappa_3 uw)-\kappa_3\kappa_4 u^2(1-uw) = f(u,w),$$

$$\dot{w} = \kappa_4(1-uw) = g(u,w), \tag{9}$$

where $k_1 = 0{\cdot}1$, $k_2 = 1{\cdot}1$, $k_3 = 0{\cdot}8$, $k_4 = 0{\cdot}8$.

Preliminary analysis of the model showed that the LC phenomenon could be obtained with diffusion of only one component. A more complicated case when both diffusion coefficients are not zeros was not investigated.

The corresponding distributed system is

$$\frac{\partial u}{\partial t} = f(u,w)+D\frac{\partial^2 u}{\partial x^2},$$

$$\frac{\partial w}{\partial t} = g(u,w). \tag{10}$$

The case was investigated with $D = 1\times 10^{-5}$. Passing to the running coordinate system, we obtained

$$\dot{u} = f(u,w)+\frac{D}{v^2}\ddot{u},$$

$$\dot{w} = g(u,w). \tag{11}$$

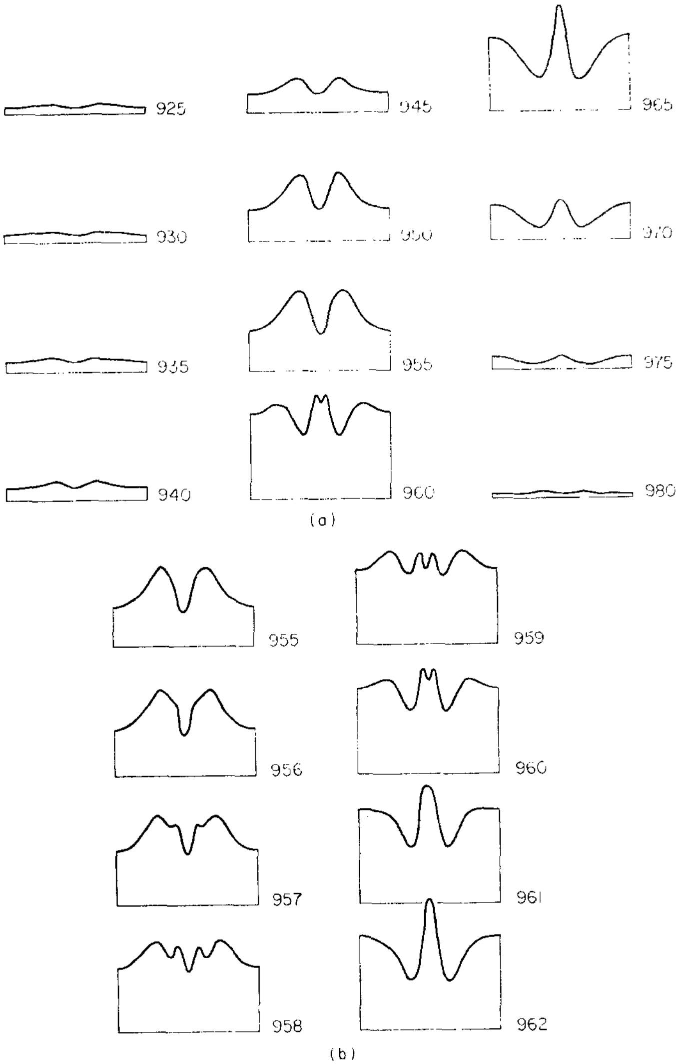

FIG. 2. Leading centre obtained in computer experiment. Abscissa is the coordinate x. Ordinate is the concentration u in system (9). (a) Series of profiles demonstrates one of the cycles in steady regime. Numbers designate time in arbitrary units after making the disturbance in the centre of the line. (b) Part of the cycle when a starter point appears.

The values of k_i in equations (9) were selected so that the oscillation period (T_v) in equations (11) was shorter than the period (T_0) in equations (9). With these values of k_i equations (10) were solved with a computer by the difference scheme:

$$\frac{\Delta u_i}{\Delta t} = f(u_i, w_i) + \frac{D}{(\Delta l)^2}(u_{i-1} - 2u_i + u_{i+1}),$$
$$\frac{\Delta w_i}{\Delta t} = g(u_i, w_i), \tag{12}$$

where $\Delta l = 0{\cdot}1$, $\Delta t = 0{\cdot}05$, $i = 1{\cdot}2\ldots n$, $n = 29$.

It was found that $T_{\mathrm{LC}} = 56{\cdot}6$, when $T_0 = 58{\cdot}7$. Figure 2 shows the concentration profiles in consecutive moments after making a local disturbance in the centre of line. The steady regime is shown (time and distance in arbitrary units).

One can see that there are two specific points disposing symmetrically with respect to the centre of line. In the points (which can be termed starter points) there arise reverse waves to the centre. The reverse wave appears at the time (t_{st}) between $t = 956$ and $t = 957$. At t_{st} in a starter point (X_{st}) equality takes place:

$$\frac{\partial u}{\partial x} = \frac{\partial^2 u}{\partial x^2} = 0. \tag{13}$$

Subsequently the point divides into maximum and minimum of unsteady waves going to the centre and from it. Figure 3 shows trajectories of maximum and minimum in u, t-space. Maximum trajectory turns into $u(t)\,|_{x=0}$. Minimum trajectory is asymptotically approaching $u_{\min}\,|_{x=\infty}$.

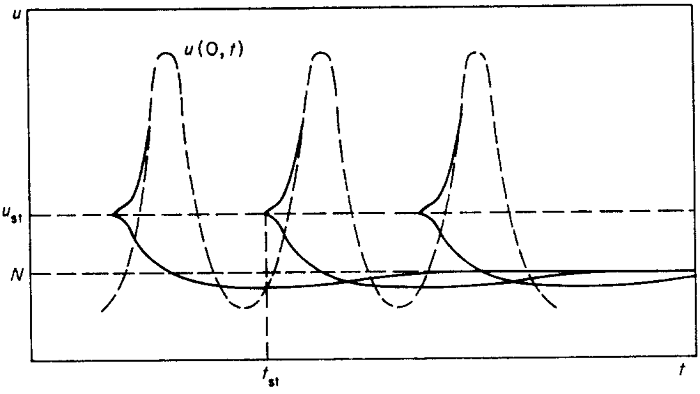

FIG. 3. Movement of extremal points in u, t-space. u_{st}, t_{st}, the coordinates of starter points in the u, t-space; $u(0, t)$, self-oscillations of u in the centre of symmetry ($x = 0$); N, minimal value of u in the stationary travelling wave.

The second approach is based on a discrete system and on limit transition to equations (4). A starting point to consider is the possibility of re-triggering two coupled monostable generators (originally the re-triggering has been termed "echo") (Krinsky & Cholopov, 1967).

(1) The crude model of monostable generator is an element which can be in one of three states: rest, excitement, refractoriness. Figure 4 shows the behaviour of the element (T_e designates time of excitement, T_R time of refractoriness).

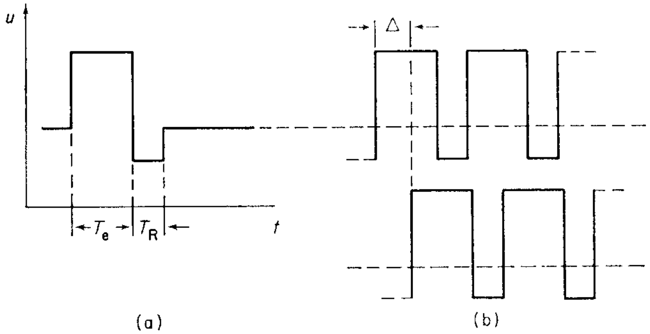

FIG. 4. Self-oscillations of two coupled monostable oscillators. (a) Pulse arising after the triggering of the generator: T_e, excited phase; T_R, refractory phase. (b) Self-oscillations under the retriggering of generators. Δ, phase shift between the generators.

Let us consider the conditions necessary for re-triggering two such elements. Let the two coupled elements rest. Then, if one element is excited, the second also becomes excited after some delay, τ. (τ may be very small and will not be taken into consideration in what follows. The condition $\tau \neq 0$ is needed for the excitement to propagate with a finite velocity along the line consisting of such elements.) The refractory element cannot be excited.

Let E_1 be excited at $t = 0$, and E_2 at $t = \Delta$. (If one introduces the phase (φ), then at $t = 0$: $\varphi_{E_1} = 0, \varphi_{E_2} = -\Delta$.) Figure 4 shows that for re-triggering it is necessary that

$$T_R < \Delta < T_e.$$

(2) Let us consider a continuous line consisting of the elements described above.

Let the initial conditions be

$$t = 0,$$

$$x > x_0, \quad u = u_e, \quad \varphi = 0,$$

$$x < x_0, \quad u = u_R, \quad \varphi = -\Delta,$$

$$T_R < \Delta < T_e.$$

Then the point x_0 becomes a periodical source of waves, analogous to the starter point.

(3) The natural way leads from models with finite number of states to the chain (or pair) of generators connected by diffusion:

$$\frac{\partial u_i}{\partial t} = f(u_i, w_i) + \frac{D_u}{h^2}(u_{i-1} - 2u_i + u_{i+1}),$$

$$\frac{\partial w_i}{\partial t} = g(u_i, w_i). \tag{14}$$

The re-triggering can be easily demonstrated in system (14) when every element has characteristics shown in Fig. 1 (case II).

Krinsky *et al.* (1971) and Shcherbunov, Krinsky & Pertzov (1972) obtained self-oscillations in such a system of diffusion-coupled monostable generators. In the first paper the necessary condition for re-triggering was discontinuity of the variable values in the neighbouring points:

$$u_{i+1}(t) = u_i(t) + \gamma(t),$$
$$|\gamma(t)| > c > 0.$$

In the second paper the LC regime remained when

$$h \to 0, \qquad u_{i+1}(t) \to u_i(t).$$

These results showed that the existence of the LC regime in equations (14) was a necessary but not sufficient condition for the existence of an LC in equations (4).

It is worth mentioning that asymmetrical LCs with one starter point arise naturally in models of one-dimensional systems. However, such regimes have not been observed experimentally. The reason may be that natural disturbances (fluctuations) are local and have symmetrical bell-shaped concentration distributions. All the artificial disturbances used hitherto were of the same type.

(C) SPIRAL WAVE—REVERBERATOR

Balachovsky (1965) considered two-dimensional space, the points of which are elements described above (Fig. 4). It has been shown that a spiral dynamical structure (reverberator) may arise in the space after breaking the wave front. Figure 5 shows the initiation of reverberator in such a model.

We have experimentally obtained a reverberator by mechanically breaking the wave front in the BFB system (Zhabotinsky & Zaikin, 1971*a*). Plate II shows a series of patterns arising after the breaking. It can be seen how free ends of fronts are twisting into a spiral. Ultimately, a steady regime settles in the reactor. There appears a region inside of which there are reverberators.

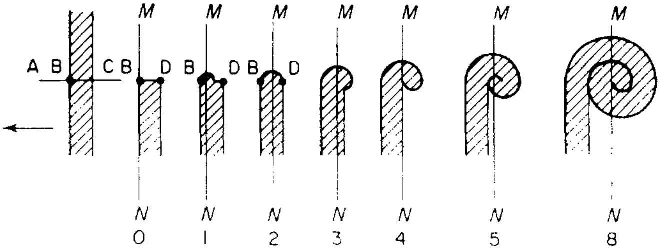

FIG. 5. Model of reverberator arising after the break of the wave front. Numbers indicate time in arbitrary units. AC is the line perpendicular to the wave front. The thick line is an active zone, a refractory zone is shaded (BD is the length of a refractory zone). The rest part of space is resting. MN is the position of the wave front at $t = 0$.

They form pairs in such a way that the external ends of the spirals are closed on each other. The region is a source of ring waves composed of the wave segments of all the reverberators. An external end of the spiral wave is either closed on another wave end to form a pair or goes setting against the reactor wall.

Winfree (1972) has independently obtained reverberators by the same procedure.

The breaking of the wave front resulting in the appearance of a reverberator may be due to different causes. Artificial breakage of the wave front may be obtained by different methods. In particular, Krinsky (1968) showed that the front may tear itself during the passage of a wave through a non-uniform part of the space. We have experimentally obtained reverberators on the boundary of artificially-made steady non-uniformity (Zhabotinsky & Zaikin, 1971*a*). Non-uniformity was made by a local decreasing of acidity.

(D) STATIONARY PERIODICAL STRUCTURE (SPS)

Turing (1952) showed that a constant in time and periodical in space structure may arise in a one-dimensional system (4) under special conditions, in particular:

$$D_u \neq D_w \neq 0. \tag{15}$$

Such structures were later investigated by Prigogine and collaborators (Prigogine & Nicolis, 1967; Prigogine *et al.*, 1969) and termed "dissipative structures". SPSs may arise in system (4) in which corresponding equations (3) describe a monostable generator, self-generator or bistable device (Poljakova, 1971).

Regimes similar to SPSs have been experimentally obtained by Busse (1969), Beck & Varadi (1971) and Herschkowitz-Kaufman (1970). Strictly speaking, all the structures were only approximately steady because of the closed

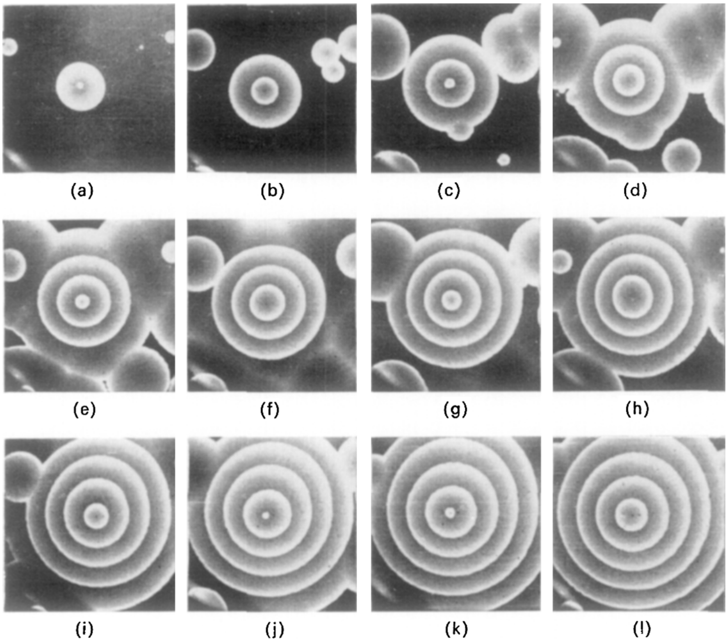

PLATE I. Leading centre. Photographs taken at 30 sec intervals. Initial reactant concentrations (mol/l): BMA = 0·16; $NaBrO_3$ = 0·23; $Fe(phen)_3$ = 0·003; H_2SO_4 = 0·27; T = 20°C.

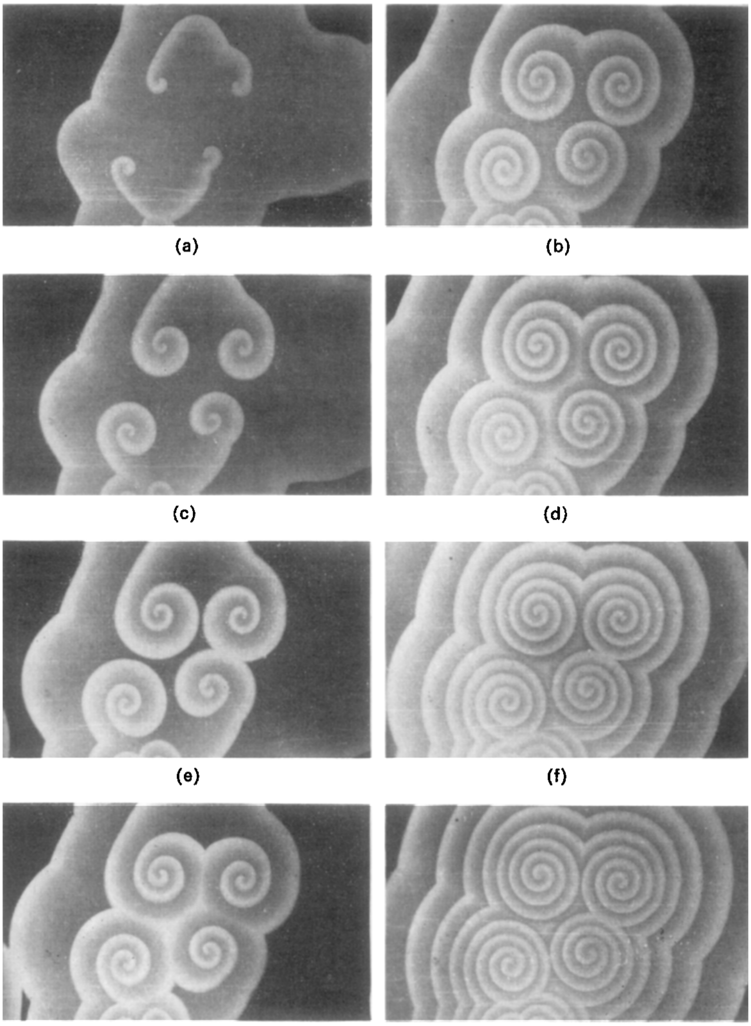

Plate II. Reverberators arising after forced break of wave front. Intervals between photographs and initial reactant concentrations as in Plate I.

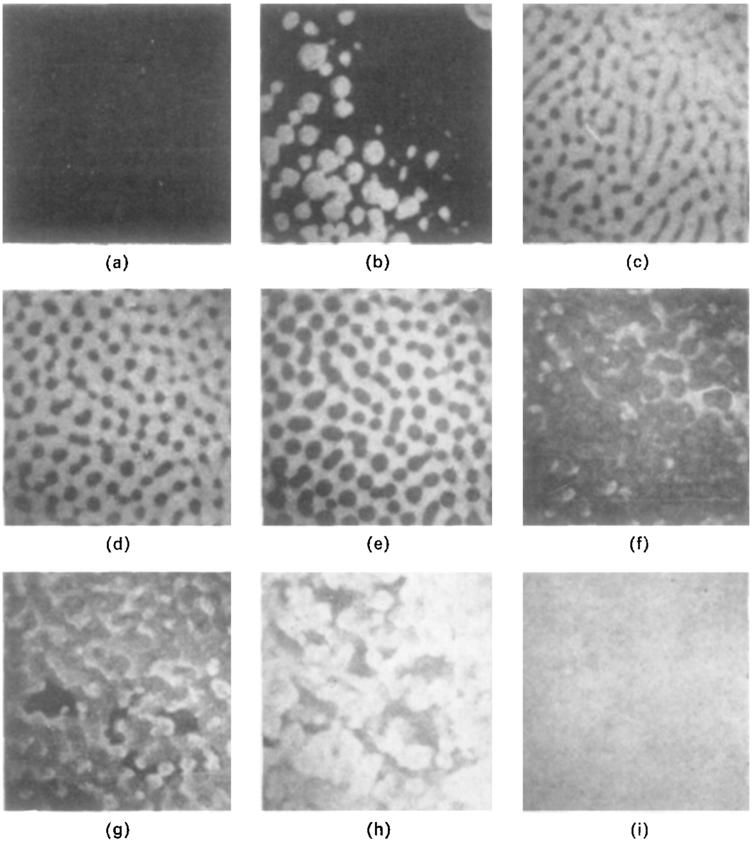

PLATE III. Small-cell structure (SPS). A series of photographs taken at two-minute intervals demonstrates the transition of catalyst from reduced (a) to oxidized (i) state. This transition is accompanied by appearance and later disappearance of spatially organized non-uniformities. Initial reactant concentrations (mol/l): acetylacetone $= 0{\cdot}05$; $NaBrO_3 = 0{\cdot}05$; $Fe(phen)_3 = 0{\cdot}0004$; $H_2SO_4 = 0{\cdot}5$.

system. Precise periodicity was not observed, one of the causes being non-stationarity of the system. SPS has been observed in vertical tubes. In the experiments of Busse (1969) and Beck & Varadi (1971) there was a gradient of the catalyst concentration. Herschkowitz-Kaufman (1970) took measures to make the initial system uniform as much as possible. However, in all cases there was an air–liquid interface where the conditions differed from those in a bulk solution. Reaction (1) usually started at the interface (more precisely, at some points of the edge angle), earlier than in the rest of the system. As a result, waves started propagating from the interface to the whole volume (from top to bottom). Thus, a periodical pattern might be a consequence of wave propagation from an LC formed on a stationary non-uniformity. A series of photographs (Herschkowitz-Kaufman, 1970) showed a typical picture of wave propagation from the part with a decreased T. Clear indications were also absent whether the observed periodical structure was motionless or not in the works of Busse (1969) and Beck & Varadi (1971).

We observed SPS in systems BFP and BFA (with acetylacetone as a reductant) in one- and two-dimensional systems. Plate III shows a series of photographs demonstrating the whole evolution of SPS. In the middle of the process [Plate III(d), (e)] the structure is approximately motionless and periodical. In a one-dimensional case a simple standing approximately periodical structure may be observed in this time interval.

In our experiments the mean space period (λ_{sp}) depended on the concentrations and not on the reactor dimensions. However, it should be pointed out that the system dimensions were usually much larger than λ_{sp}, the system was not steady and the periodicity was approximate.

In the upper half of Plate III(e), 185 distances between the centres of the neighbouring reduced parts have been measured. Statistical processing gave the following result:

$$\lambda_{sp} = 2{\cdot}5 \pm 0{\cdot}04 \text{ mm.}$$

The distribution differed slightly from a normal one and was unsymmetrical. This is probably the consequence of non-stationarity of the system.

SPS did not usually arise over the entire space, but in some parts from which it spread over the whole reactor. Elements of the structure were observed earlier when space propagation of autocatalytic reaction (1) was studied by Vavilin (1971). Under particular conditions centres of oxidation arose at some distance ahead of the front of reaction. They then increased becoming one with the zone of oxidation.

In the pure form, SPSs described above took place in the region of parameters where BO and LC were absent. There was a narrow parametric zone where LCs and SPS coexisted. SPS appeared in the region of BO at the moments of transitions into an oxidized state.

3. Discussion

Summarizing the results of the present and earlier papers, one can see that steady regimes exist in non-linear distributed systems with diffusion-type coupling, their characteristics being independent of the initial conditions. Dependance on the initial conditions is only the fact of existence of certain types of structures. The well known structures are:

(i) single travelling wave (steady only in the running co-ordinate system);
(ii) travelling waves in ring systems (Poljakova, 1971; Bullock & Horridge, 1965; Wiener & Rosenblueth, 1946);
(iii) Turing's structures.

However, the shapes of waves travelling in a ring and of Turing's structures are closely connected with the geometry of the system as a whole. If the processes are periodic in space the relations take place:

(a) for waves travelling in a ring

$$\lambda = \frac{L}{n},$$

(b) for Turing's structures

$$\lambda = \frac{2L}{n},$$

where λ is wavelength, L is system length and n is a whole number. From here one can obtain the expression for oscillation period in ring system:

$$T = \frac{L}{nv},$$

where v is wave velocity.

In the present paper steady AWPs are described with characteristic λ and T depending on neither initial nor boundary conditions. These are the leading centre and reverberator. In these two cases steady oscillations occur in every point of space. The position of the central part of the influence zone of AWPs is fixed in space and depends on the initial conditions only. (Space localization of structures described by Prigogine & Nicolis (1971) was determined by spatial gradient of the system parameter.) In principle, such AWPs may settle their own position in infinite uniform space. There is a steady distribution of oscillation phase in the central part of the AWP zone. AWPs resemble Liesegang rings and figures of crystal growth with the difference that they are formed by stationary distribution of oscillation phases rather than concentrations.

It is necessary to introduce clarity in the statement about characteristic λ and T. In the experiment in case of reverberator, λ_R and T_R are constant with high precision, because the values are defined by refractory time in case of triggering by amplitude equal to the own one. This amplitude is much larger than values of concentration fluctuations.

The oscillation periods in our system form the following series

$$T_R < T_{LC} < T_0.$$

In the LC case dispersion of T_{LC} (consequently λ_{LC}) is very large. This may be due to the fact that LCs often make their appearance at microheterogeneities. This supposition is confirmed by the fact that the oscillation period of LCs arising in the edge angle is frequently much shorter than average T_{LC}.

In general, the role of fluctuations and microheterogeneities in the LC initiation is probably the same as in the process of formation of a new phase from the metastable one. Indeed, an LC arises when a threshold has been exceeded due to a fluctuation. On a microheterogeneity the threshold may be lowered.

It should be emphasized once again that under certain conditions LCs and reverberators arise only as a result of fluctuations exceeding some threshold value, i.e. in the system in which the initial state is stable according to Liapounov.

The relation of observed SPS to Turing's structures is unclear as yet. In particular it should be elucidated whether the loss of stability of space—uniform state occurs by Turing's mechanism or not and whether the space period is affected by boundary conditions.

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APPENDIX

Korzoohin's Theorem (Korzoohin, 1967)

It is known that a system of ordinary differential equations with arbitrary polynomials on the right-hand sides of (A2) may be a model of the dynamic behaviour of any complexity. Korzoohin has shown that a "chemical" system of equations can always be constructed with solutions asymptotically approximating to the solutions of a given system (A2). Thus any complex behaviour can be realized in principle in a homogeneous chemical system. Below is given a short formulation of the Korzoohin theorem.

A chemical system can be represented by the following system of equations:

$$n_i = \beta_i^{\kappa} n_{\kappa} + \gamma_i^{\kappa l} n_{\kappa} n_l \tag{A1}$$

where

(1) all the $n_i \geqslant 0$,

(2) $\sum \mu_i n_i = const.$,

$$(3)\quad \beta_i^{\kappa} = \begin{cases} 0 \\ |\beta_{\kappa}^{\kappa}|, \end{cases} \qquad \gamma_i^{\kappa l} = \begin{cases} 0 \\ |\gamma_{\kappa}^{\kappa l}|, \end{cases} \qquad \gamma_{\kappa}^{\kappa l} = \gamma_l^{l\kappa}, \qquad \beta_{\kappa}^{\kappa} \leqslant 0, \qquad \gamma_{\kappa}^{\kappa l} \leqslant 0,$$

where n_i are concentrations, β_i^{κ}, $\gamma_i^{\kappa l}$ are rate constants, and μ_i are molecular weights.

Theorem: Let a system be given

$$x_i = A_i(x), \tag{A2}$$

where $A_i(x)$ are arbitrary polynomials with whole non-negative indices. A chemical system (A1) can always be constructed with the parameter $1/\varepsilon$ being a multiplier in some rate constants so as

$$x_i(t) \to n_i(t) + 0(\varepsilon)$$
$$\text{if} \quad \varepsilon \to 0.$$