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NONLINEAR PHENOMENA IN OSCILLATORY SYSTEMS OF HOMOGENEOUS REACTIONS – EXPERIMENTAL OBSERVATIONS

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An oscillating system of homogeneous chemical reactions (oxidation of malonic acid by bromate with ceric/cerous ion system as the catalyst) was followed experimentally in several reactor configurations, operated both as close and open systems. Characteristic nonlinear phenomena observed include: damped oscillations of concentrations of reaction components in a well stirred batch reactor, undamped oscillations and sudden changes of oscillatory behaviour (jump to a new steady state) in CSTR, and interaction of oscillations in the two connected CSTR's. In a tubular reactor stationary and travelling concentration waves were observed. In the system of CSTR connected with a tubular reactor spreading of waves from CSTR to the tubular reactor, and vice versa was followed. In the flow through tubular reactor the formation of non-monotonic concentration profiles was measured, which were basically stationary with respect to changing flow-rate. The course of oscillations in CSTR was simulated on the basis of a semiempirical reaction kinetics model. An attempt to simulate quantitatively the behaviour of the distributed system with the common type of Fickian diffusion balance equations failed. Difficulties in the proper description of the transport of ions through the concentration gradient and the gradient of the electrical potential found in this system are discussed.

1. Introduction

Interaction of oscillating chemical reactions and transport processes can give rise to a number of interesting time and/or space dependent concentration patterns. For example, damped and undamped oscillations of concentrations of characteristic components can occur in the closed and opened lumped parameter systems. In distributed systems stationary and travelling concentration waves and stable, stationary space dependent non-monotonic concentration profiles (dissipative structures) were predicted [1]. A number of theoretical papers on this subject written from the point of view of nonlinear thermodynamics (cf. survey by Nicolis [2]) and theoretical biology (cf. Zhabotinski and Zaikin [3]) has appeared recently. Two symposia on the subject of oscillatory processes in biological and chemical systems have been held in the Soviet Union [4,5]. Most of the experimental work is based on observation of concentration changes in the Belousov–Zhabotinski reaction, the oxidation of malonic (bromomalonic) acid by bromate in the presence of ceric (cerous) ions in sulfuric acid. Studies include observations of oscillatory behaviour in a batch well mixed system [6] and qualitative observations in a quasi-one-dimensional and quasi-two-dimensional systems [7–12]. Tatterson and Hudson [13] reported on an experimental study of chemical wave propagation using a tubular system attached to the stirred tank reactor operated batchwise. The stirred tank functioned as a wave source and at one chosen set of experimental conditions (frequency of oscillations of the order of 1 min^{-1}) the authors studied the characteristics of the emitted waves (wavelength, frequency, speed) in dependence on time, position along the tube, and the rate of stirring. The wave characteristics did not change greatly as the wave propagated down the tube; the wave speed increased slightly with increasing frequency and was of the order of 0.5 cm min^{-1}.

However, most of the above experimental studies used closed (batch) systems. In agreement with the actual situation in biological systems, theoretically oriented papers usually consider open systems with fixed concentrations of certain precursors (which are, e.g., kept constant by exchange of matter with environment in cells, tissues, etc.) (cf. survey by Nicolis and Portnow [24]).

Here we shall present experimental results obtained mainly in the open, both lumped and distributed, parameter systems, illustrating the above mentioned theoretically predicted characteristic phenomena. To our knowledge such *quantitative* experimental observations on open model systems are reported for the first time in the literature. Detailed information on the kinetics of the Belousov–Zhabotinski reaction can be found in a recent book by Zhabotinski [33] and a review article published by Noyes and Field [34].

2. Experimental results

2.1. Lumped parameter systems

In fig. 1. the glass tank reactor which could be operated batchwise or continuously and was also used as part of the cascade of reactors is shown. Additional details on the experiments can be found elsewhere [14,15].

The temperature in the reactor was held constant at the chosen value by means of flow through a cooling jacket. The reaction mixture was mixed intensively. The intensity of mixing was kept at such a level, that its further increase did not affect the course of oscillations (usually 500 r.p.m). Three different reactor sizes (18 ml, 100 ml, 200 ml) with different reaction mixture volume to wall area ratio were used. No effect of the walls on the course of oscillations was observed under the conditions given. During the course of experiments the oxidation–reduction potential in the reactor was continuously monitored using Pt and calomel electrodes (with the potassium sulfate electrolyte bridge). The change in electrical potential corresponds to the change in the ratio of concentrations Ce^{4+}/Ce^{3+}. The concentration of the bromide ions was followed by means of a selective membrane electrode.

Each experiment was started at chosen values of temperature and concentration as batch experiment, by adding cerous and bromate salts to the reaction mixture consisting of malonic acid and sulfuric acid. In continuous flow experiments two separate continuous inlet streams, first formed by the mixture of cerous and bromate ions and second by the mixture of malonic acid and sulfuric acid were used. The concentrations were chosen in such a way, that the resulting inlet concentrations after mixing were equal to the actual working concentrations in the reactor.

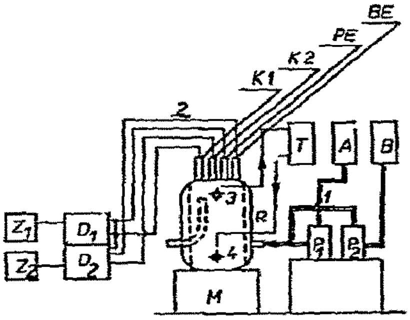


Fig. 1. Stirred tank reactor (CSTR) used for experiments. R: Reactor; M: magnetic stirrer; K_1, K_2: calomel electrodes; PE: Pt electrode; BE: bromide selective membrane electrode; P_1,P_2: pumps; T: thermostat; Z_1, Z_2: recorders.

2.1.1. Oscillations in a batch reactor

The steady state in a batch reactor is always stable. In reaction system with linear kinetics the number of extrema of concentration values around the steady state will be comparable with the number of reaction components present in the system. In the case of a Belousov reaction with highly nonlinear kinetics relations, the number of oscillations can be far higher. In the case shown in fig. 2 the overall number of oscillations was over 80.

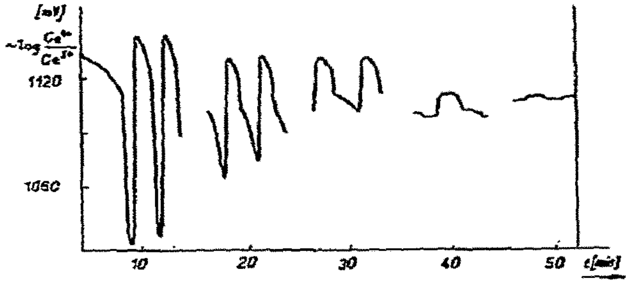


Fig. 2. Successive decay of oscillations in the batch reactor. Initial concentrations: 0.063 M $KBrO_3$, 0.032 M malonic acid, 10^{-3} M Ce^{4+}, 3N H_2SO_4 (all experiments). Total number of oscillations: 80. Temperature 40°C (common for all experiments except where stated otherwise).

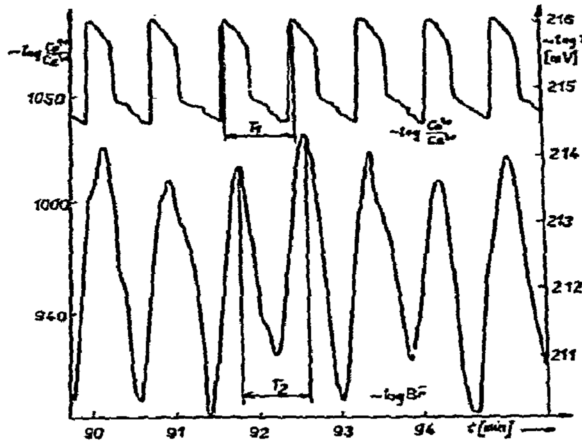


Fig. 3. Continuous course of oscillations in CSTR. Initial and inlet concentrations: 0.5 M $KBrO_3$; 0.032 M malonic acid; 10^{-3} M Ce^{4+}; T = 25°C. Reactor volume: 200 ml. Flow-rate: 139 ml/hour. Oscillation periods: T_1 = 63 s(Ce^{4+}/Ce^{3+}); T_2 = 63 s(Br^-).

2.1.2. *Continuous stirred tank reactor*

In CSTR unique or multiple steady states can exist, in dependence on the values of the system parameters. Some of the existing steady states can be unstable. If the unstable steady state is unique, then undamped oscillations in the concentrations of characteristic components can be followed in CSTR. Such a situation is illustrated in fig. 3, where the oscillatory course of concentrations of Ce^{4+}/Ce^{3+} ions and Br^- ions is depicted. Starting from different initial compositions, the concentration trajectory will ultimatelly evolve to the course shown in fig. 3.

An effect of changing flow rate on the character of oscillations is illustrated in fig. 4. The period of oscillations increases with the decreasing reactor residence time τ ($\tau = V/F$, see later), due to the changed concentration of certain reaction intermediates. Variations of the flow-rate can thus be used as a means of generating oscillations of different shapes and frequencies. Composed oscillations can be also obtained; some of the regimes observed are depicted in fig. 5.

At a certain flow-rate and initial concentrations of reactants we can experimentally follow the situation, where at a certain time of evolution of the concentration trajectory one oscillatory regime changes abruptly into another one (see fig. 6) or into a non-oscillatory regime (see fig. 7), after only a slight perturbation in the values of concentrations of the active components. This could correspond in the theoretical description to the existence of two unstable steady states with limit cycles surrounding each of them or to the existence of one stable and one unstable steady state. It is improbable, that a slight perturbation in the concentration of the reactors could cause a change in the reaction mechanism.

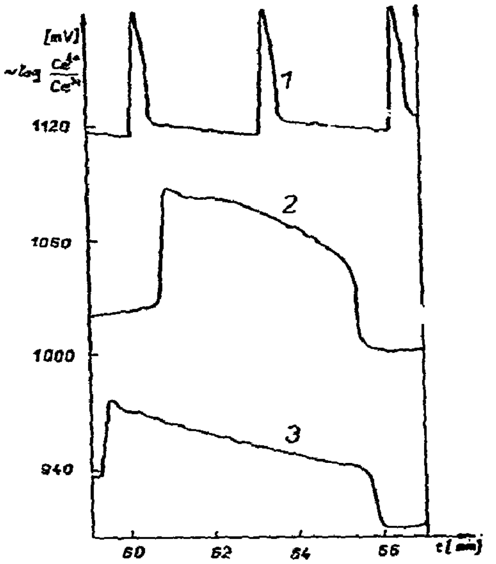


Fig. 4. Effect of flow-rate (F) on the form of oscillations. Initial and inlet concentrations: 0.01 M $KBrO_3$, 0.032 M malonic acid, 10^{-3} M Ce^{4+}, CSTR, V = 200 ml. (1) Batch reactor (F = 0); (2) CSTR (F = 1100 ml/hour); (3) CSTR (F = 2200 ml/hour).

2.1.3. *Two connected CSTR's*

Two reactors connected by a short tube (enabling partial exchange of the reaction mixture) can serve as a simple model of interactions of two oscillating systems. In fig. 8, oscillations in the reactor forming a member of the two-stage cascade with those for a single reactor under identical conditions are compared. The frequency of the oscillations in the cascade is four times lower than that in a single reactor. Theoretical analysis made by Ruelle [16] shows, that if two systems with periodic solutions with a rational ratio of periods interact (here we start with two systems of the same period) then the final solution can be periodic with a period close to the integral multi-

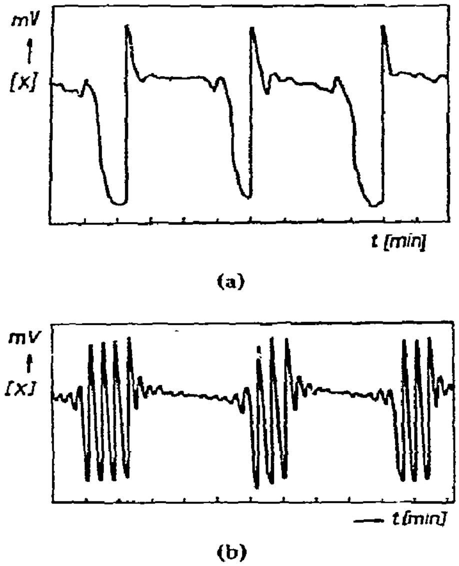


Fig. 5. Composed forms of oscillations generated in CSTR during the transient period. Initial and inlet concentrations:
(a) 0.01 M $KBrO_3$; 0.032 M malonic acid, 0.0002 M Ce^{4+}, V = 200 ml; F = 500 ml/hour;
(b) 0.025 M $KBrO_3$; 0.066 M malonic acid; 0.0002 M Ce^{4+}, V = 200 ml; F = 500 ml/hour.

ples of the original periods. This result seems to be supported by the above experiment.

2.2. *Distributed systems*

A tubular reactor connected with a well mixed reactor, where both reactors can be operated either batch-wise or as flow-through systems is shown in fig. 9. Concentration changes were followed by means of Pt electrodes built into the walls of the tubular reactor and the course of concentrations along the tubular reactor was recorded simultaneously with the concentration changes in the stirred tank. Details of the experimental arrangements were reported elsewhere [15]. In the following we shall illustrate and briefly discuss the individual characteristic regimes observed in the system.

Transport processes can cause, that an originally unstable steady state in the well mixed reactor will become stable in the tubular reactor. This can be realized experimentally in such a way, that in the well stirred system undamped oscillations will be observed, but, on the contrary, we shall observe monotonic concentration trajectory in the tubular reactor, provided that both systems evolved from the same starting point. Such a case is depicted in fig. 10. However, under different experimental conditions also the reversed situation was observed experimentally (see fig. 11). Here the transport processes taking place in the tubular reactor destabilize the steady state originally stable in the well mixed system.

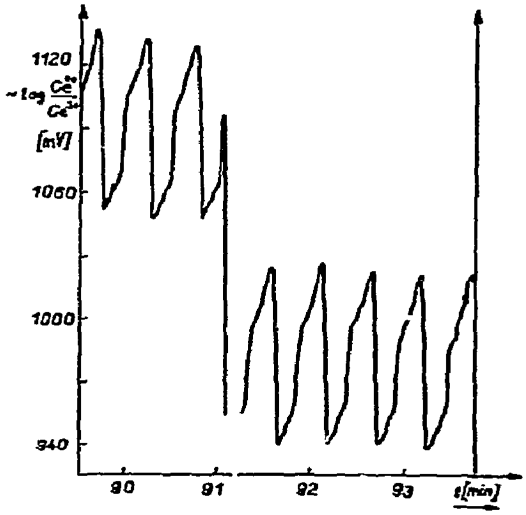


Fig. 6. CSTR: Change from one oscillatory regime to another. Initial and inlet concentrations: 0.063 M $KBrO_3$; 0.032 M malonic acid; 10^{-3} M Ce^{4+}; V = 200 ml; F = 1100 ml/hour.

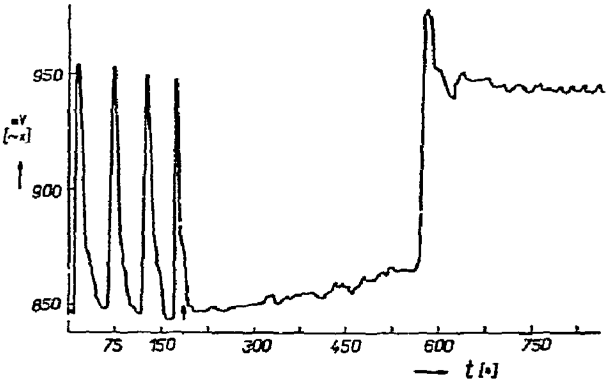


Fig. 7. CSTR: Change from an oscillatory to a non-oscillatory regime. Initial and inlet concentrations: 0.01 M $KBrO_3$; 0.032 M malonic acid; 0.0002 M Ce^{4+}; V = 200 ml; F = 600 ml/hour.

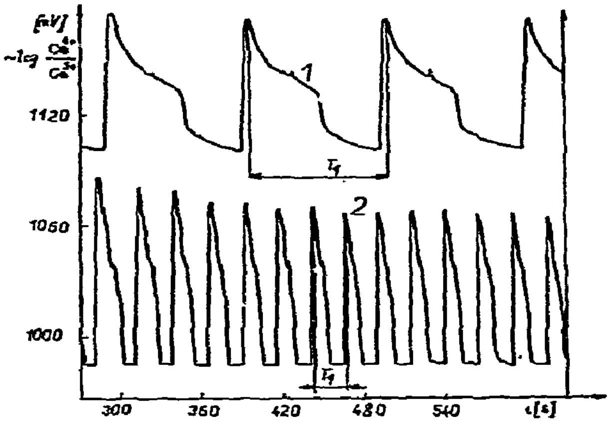
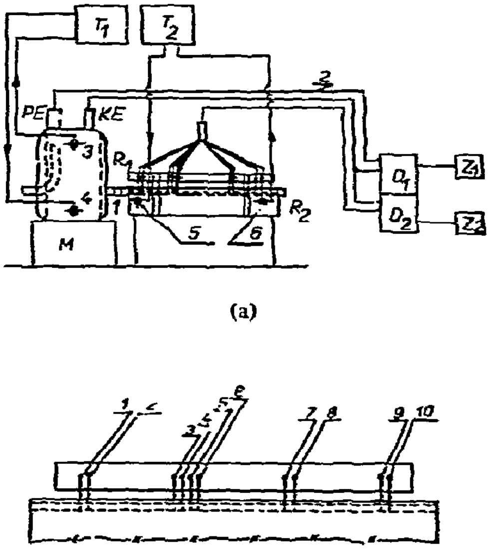


Fig. 8. Comparison of oscillations in a single reactor (curve 2) and the reactor forming part of a reactor cascade (curve 1). Initial and inlet concentrations: 0.01 M $KBrO_3$; 0.032 M malonic acid; 10^{-3} M Ce^{4+}. Periods: T_1 = 105 s (cascade); T_2 = 25 s (single reactor).



(a)

(b)

Fig. 9. (a) Experimental system of stirred tank and tubular reactor: R_1: stirred tank reactor; R_2 tubular reactor; Z_1,Z_2: recorders; M: magnetic stirrer; PE: Pt electrodes; KE: calomel electrode; T_1,T_2: thermostats; 1: connection between stirred tank and tubular reactors.

(b) Location of measuring points. Distance between electrodes: 1–2, 3–4, 5–6, 7–8, 9–10: 2 mm; 2–3, 6–7, 8–9: 4 cm.

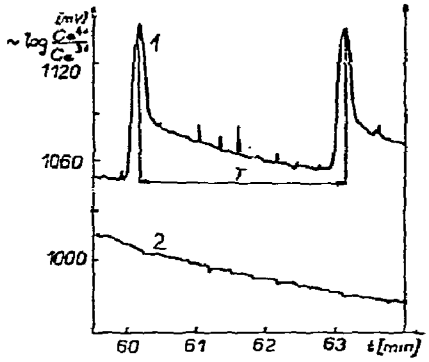


Fig. 10. Stabilization of the steady state in the tubular reactor: (1) stirred tank reactor; (2) tubular reactor, measuring point no. 5 (characterizes the behaviour at other points also). Initial and inlet concentrations in CSTR: 0.01 M $KBrO_3$; 0.032 M malonic acid; 10^{-3} M Ce^{4+}.

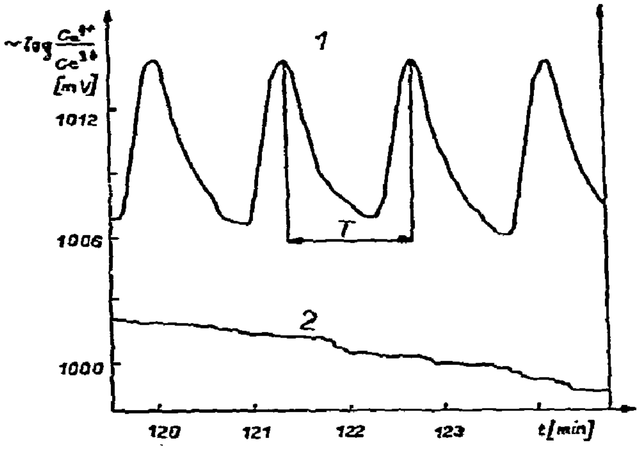


Fig. 11. Oscillations in the tubular reactor compared with a monotonic concentration trajectory in CSTR: (1) tubular reactor, measuring point no. 4; (2) CSTR. Initial and inlet concentrations: 0.14 M $KBrO_3$; 0.3 M malonic acid; 10^{-3} M Ce^{4+}; 0.00125 M ferroin.

The oscillatory course of reactions in the tubular reactor can be of various character. However, from the experimental point of view, we can principally find two different characteristic regimes:

(a) oscillations variable in time and position, and

(b) stationary oscillations.

In case (a) we can further differentiate between oscillations, which take place in CSTR and tubular reactor without mutual interactions and between oscillations in the form of advancing waves.

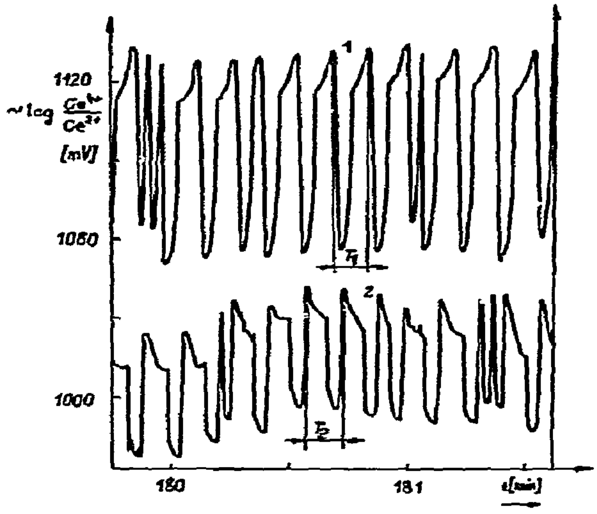


Fig. 12. Comparison of the course of oscillations at different positions in the tubular reactor: (1) measuring point no. 9; (2) measuring point no. 10. Oscillation periods $T_1 = T_2 = 16$ s. Initial and inlet concentrations: 0.01 M $KBrO_3$; 0.032 M malonic acid; 10^{-3} M Ce^{4+}.

Oscillations in tubular reactor with characteristics variable in time and space are shown in fig. 12. As follows from the more detailed study which is now in progress, under these experimental conditions the oscillations usually nearly repeat themselves in time and space (i.e., when comparing oscillations in different experimental points they nearly repeat after a certain interval of time has elapsed). Oscillatory waves advancing from the stirred tank into the tubular reactor are depicted in fig. 14. We can observe, that the course of oscillations in the tank reactor is nearly the same as the course of oscillations at the end of the tubular reactor (inhibitor KBr was added into the tank reactor to create the particular character of the oscillations). It appears, that the rate of advancement of the concentration waves under this particular conditions was of the order of magnitude of cm/s. More quantitative study is now under way.

The reversed situation, where fast oscillations within the tubular reactor advance into the stirred tank (with its own oscillatory frequency) are shown in fig. 13.

Under certain experimental conditions oscillations in the tubular reactor change their character into slowly varying changes going up an down (see fig. 15).

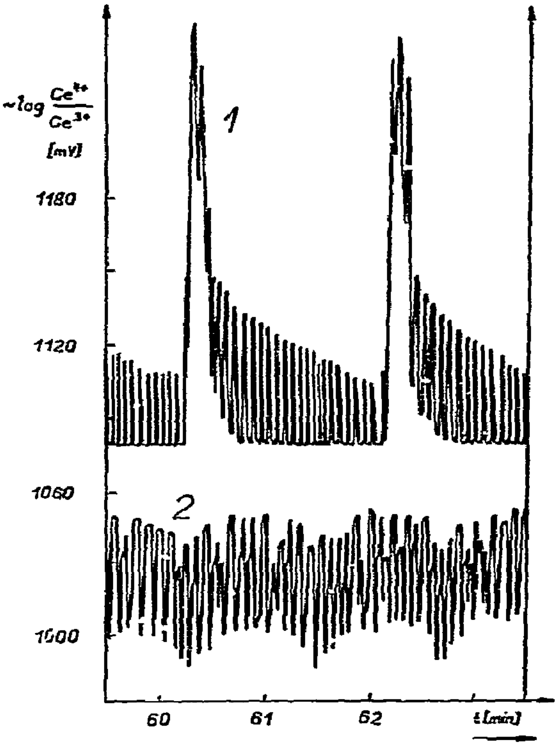


Fig. 13. Propagation of oscillation waves from batch to tubular reactor: (1) batch reactor; (2) measuring point no. 1, tubular reactor. Initial and inlet concentrations: 0.01 M $KBrO_3$; 0.032 M malonic acid; 10^{-3} M Ce^{4+}.

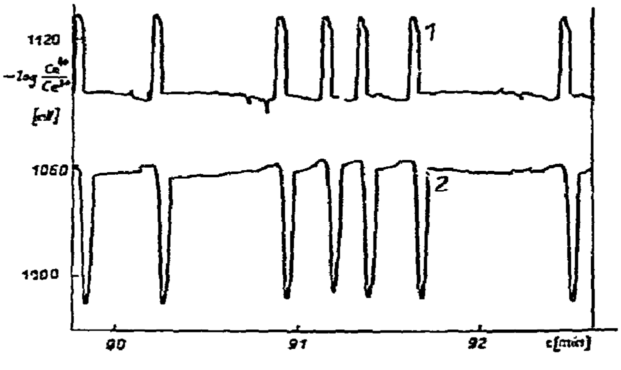


Fig. 14. Propagation of oscillation waves from CSTR to tubular reactor: (1) tubular reactor, measuring point no. 10; (2) CSTR reactor. Initial and inlet concentrations: 0.01 M $KBrO_3$; 0.032 M malonic acid; 10^{-3} M Ce^{4+}; $V = 200$ ml; $F = 2200$ ml/hour.

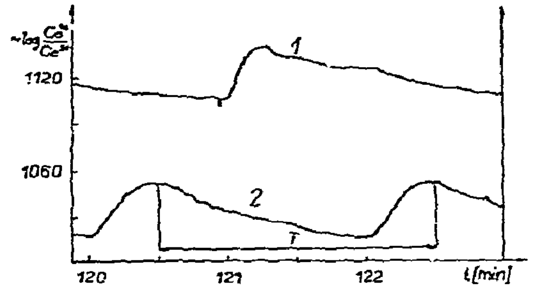


Fig. 15. Slowly varying concentrations in the tubular reactor: (1) tubular reactor, measuring point no. 5 (period T_1 = 3.5 min); (2) tubular reactor, measuring point no. 2 (period T_2 = 2 min). Initial and inlet concentrations: 0.01 M $KBrO_3$; 0.032 M malonic acid; 0.001 M Ce^{4+}; traces of Br^- into CSTR. CSTR: V = 200 ml; F = 2200 ml/hour.

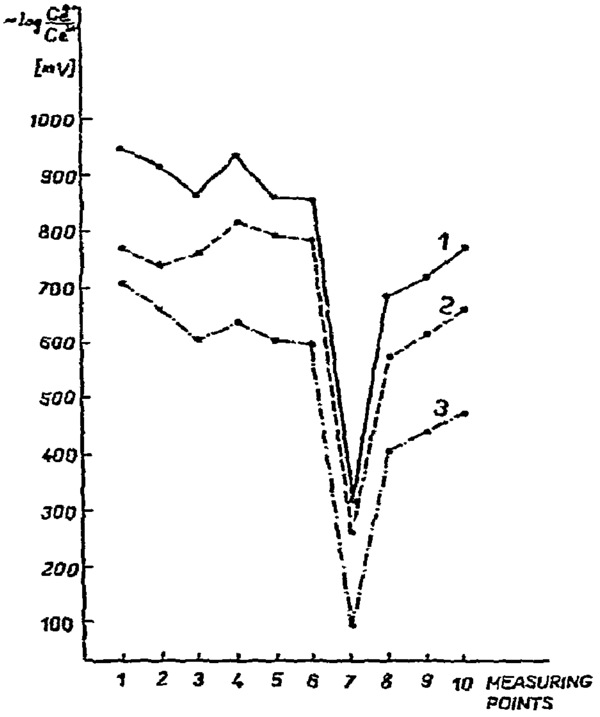


Fig. 16. Nonmonotonic stationary concentration profiles as function of the flow-rate. Tubular reactor: (1) flow-rate F_1 = 1824 ml/hour, $\bar{v}$ = 11.3/s; (2) flow-rate F_2 = 648 ml/hour, $\bar{v}$ = 4.0 cm/s; (3) flow rate F_3 = 2292 ml/hour, $\bar{v}$ = 14 cm/s. Initial and inlet concentrations: 0.01 M $KBrO_3$; 0.032 M malonic acid; 0.001 M Ce^{4+}.

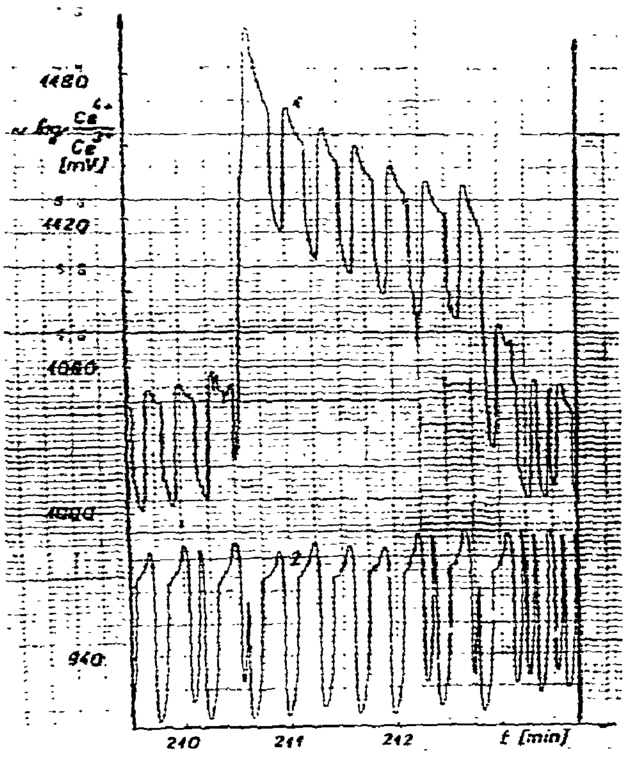


Fig. 17. Comparison of the oscillatory course of the concentration in CSTR (curve no. 1) and the tubular reactor (curve no. 2) under flow-through conditions. Flow rate in CSTR: F = 1514 ml/hod, reactor volume V = 200 ml. Flow rate in tubular reactor: F = 786 ml/hod. Initial and inlet concentrations: 0.01 M $KBrO_3$; 0.032 M malonic acid, 0.001 M Ce^{4+}.

This resembles in character the standing waves.

Under flow-through conditions we could observe in the tubular reactor longitudinal, nonmonotonic concentration profiles which varied with position but were constant in time. This type of profiles which resembles dissipative structures (Glansdorff und Prigogine [1]), is shown in fig. 16 for three different flow-rates. When considering the effect of the flow-through conditions on the course of concentration trajectories in the tubular reactor, we have to keep in mind that the mean residence time in the experiments depicted in fig. 16 was 1–3 s. It means, that this residence time was comparable to the reaction half-time of the fast reactions of the oscillation cycle and that interactions between flow and reactions are plausible. Under comparable reaction and flow-through conditions an oscillatory course of solutions was also observed, see fig. 17 (flow-rate in the tubular reactor $F = 786$ ml/hour Hence the oscillatory regime can exist also under flow-through conditions (i.e., the effect of flow and convection does not change the basic character of the reaction–diffusion system).

3. Theoretical

3.1. Lumped parameter systems – Mass balances

Let us consider a cascade of N continuous well mixed stirred tank reactors where R independent chemical reactions between S components take place. To describe the time course of the concentrations of the S components we have to solve R mass balance equations. The concentration C_{ij} of the ith component in the jth reactor is described by the relations

$$\mathrm{d}(C_{ij}V_j)/\mathrm{d}t = F_{j-1}C_{ij-1} - F_jC_{ij} + \sum_{r=1}^{R} \nu_{ir}R_{ijr}V_j = G_j, \tag{1}$$

with initial conditions:

$$t = 0: \qquad C_{ij} = C_{ij}^0. \tag{2}$$

F_{j-1}, F_j represent inlet and outlet stream volumetric flow rates, V_j reactor volume, and the term $\Sigma_{r=1}^{R}\nu_{ir}R_{ijr}V_j$ describes the overall source term of the component i due to R independent reactions. Concentrations of remaining $S - R$ components can be determined from the initial and inlet conditions (or corresponding linear differential relations).

In the steady state, when $V_j = \text{const}$, $F_{j-1} = F_j = \text{const}$, we obtain a set of $N \times R$ steady state balance equations

$$C_{ij-1} - C_{ij} = -\tau_j \sum_{r=1}^{R} \nu_{ir}R_{ijr}. \tag{3}$$

Zhabotinski et al. [17] proposed a system of two semiempirical equations for the description of the oscillatory behaviour of the concentration of characteristic components (x – concentration of ceric ions, y – concentration of unidentified reaction intermediate, probably BrO):

$$\dot{x} = y\,(1 - x) - \delta x, \tag{4}$$

$$\dot{y} = (y/\epsilon)\,\{1 - x[1 + \alpha + (y - \alpha)^2]\} + 1. \tag{5}$$

The parameters α, ϵ, $\delta = \gamma/\beta$, are functions of the concentrations of malonic acid, bromate and total ceric/cerous ion concentrations. It can be shown, that this model predicts a unique unstable steady state in the region of the experimentally observed oscillations [18]. By means of the empirical fitting of parameters, reasonable agreement between experimentally observed and simulated oscillatory trajectories can be attained, which is illustrated in fig. 18. From the point of view of numerical mathematics the system of eqs. (1) and (2) represents a system of stiff equations and efficient numerical methods have to be used.

However, the unique steady state predicted does not agree with experimental observations. These require that under certain experimental conditions, more steady states, some of them unstable to small concentration perturbations, would be predicted by the model.

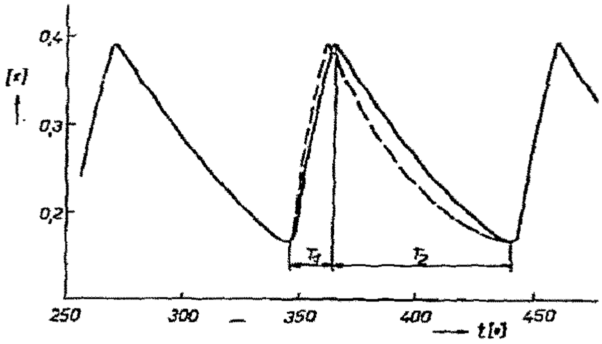


Fig. 18. Comparison of experimental (dashed line) and simulated (full line) course of oscillations in CSTR (x – dimensionless concentration of Ce^{4+}). Initial and inlet concentrations: 0.01 M $KBrO_3$; 0.032 M malonic acid; 10^{-3} M Ce^{4+}. Computed half-periods: $T_1 = 18$ s, $T_2 = 76$ s. Experimental half-periods: $T_1 = 15$ s, $T_2 = 75$ s. $\alpha = 0.196$; $\beta = 0.01$; $\gamma = 0.016$; $\epsilon = 0.005$.

Detailed study of the kinetics mechanism of the Belousov reaction was completed recently by Noyes and coworkers (Field et al. [19]). The simplest kinetic scheme which can be used for simulation, comprises three independent components and enables one to obtain a wider spectrum of oscillatory trajectories. Comparison of the simulated and experimental trajectories, which is under study, will hopefully bring proper relations for model parameters and hence improvement of the description of the more complex forms of the trajectories observed. The main requirement on the model would be that it should allow predictions of multiple unstable steady states under different operating conditions.

3.2. Distributed systems

The effect of diffusion on the course of concentration trajectories in situations where in the corresponding lumped parameter case we shall deal with unique or multiple steady states some of which are unstable, has been dealt with in the recent literature. Studies using analytical methods and linearization techniques (e.g., Gmitro and Scriven, [20]; Othmer and Scriven [21]; Edelstein, [22]), as well as computational studies (cf. Nicolis [2]; Goldbeter [23]) were reported in the literature (see also the survey by Nicolis and Portnow [24]). For example, the computational study published by the author [25,26] revealed the existence of travelling waves and undamped oscillations of temperature and concentration of active reaction components in spherical catalytic system, described by the balance relations given by eq. (6). Examples both for a unique unstable steady state and multiple steady states were given in the papers. Ortoleva and Ross [27] have studied recently a variety of chemical wave phenomena which can arise in the systems described by eq. (6). They used perturbation techniques and determined analytically various characteristics of chemical waves in the cases with low frequency, long wavelength and small amplitude waves. They have also studied the heterogeneous effects on the kinetics due to gradients or localized points of reaction. However, it seems, that their results are not applicable to relaxational types of oscillations which are predicted by the models of Belousov reaction.

Koppel and Howard [28] have studied kinematic waves which can arise if an external gradient of concentration (or temperature) is imposed on a chemical limit cycle. They have verified experimentally, that in the case of the Belousov reaction we can meet with the kinematic waves when the concentration gradient of one of the reactants is formed initially. They have questioned the existence of a steady-state, space dependent regime in the Belousov reaction. Nicolis and Auchmuty [29] studied a model chemical network involving reaction and diffusion. They have found spatially and temporarily ordered solutions by applying bifurcation theory and calculated them analytically in an approximate way and thus proved their existence. When a certain critical value of the bifurcation parameter was exceeded (e.g., concentration of one of the reactants) then existence of several stable steady states so-called dissipative structures, was possible.

If such a variety of dissipative structures would exist in experimentally studied systems, then the exact form of the concentration (and/or temperature) trajectory in phase space (i.e., history in time) will determine, which of the dissipative structure will be achieved. If we are in the neighbourhood of critical (bifurcation, branching) point, then even slight disturbances in the concentration trajectory can cause that different steady states (or wave-form) solutions are achieved. Hence the reproducibility of the experimental results obtained under such conditions is questionable. Quantitative study of the above wave-like and dissipative structures phenomena would then, in our opinion, require simultaneous solution of proper mass, momentum and enthalpy balance equations with reproducible experimental verification of the different phenomena predicted. However, the first obstacle which arises in the application of the above procedure to the Belousov reaction is the insufficient knowledge of the detailed kinetic mechanism.

Problems also arise in the numerical simulation of the system of nonlinear partial differential equations of the parabolic type

$$\partial \mathcal{C}/\partial t = f(\mathcal{C}) + \mathcal{D}\nabla^2\mathcal{C}, \qquad (6)$$

where $\mathcal{C}$ denotes the vector of characteristic components, $\mathcal{D}$ the matrix of diffusion coefficients (usually diagonal), and $f(\mathcal{C})$ the reaction rate function. If we discretize the above system of PDE in the space variables we obtain the system of ODE which are of the stiff character for the relaxational types of oscillations described by models of the Belousov reaction.

Efficient numerical algorithms for solution of the "stiff" PDE remain to be devised.

Attempts to simulate the behaviour of the above presented characteristic nonlinear phenomena observed in the tubular reactor do not give satisfactory results. Diffusion coefficients used were of the order of magnitude of 10^{-5} cm^2/s and a semiempirical description of the oscillatory mechanism [eqs. (4), (5)] was used.

A principal difficulty stems further from the fact, that the common form of the transport equations including only diffusion and convection terms will not describe this system properly. The change of concentration of characteristic components, which are of ionic character, brings with itself the space and time changes of the electric potential and this will affect the rate of transport of the ionic components.

Several possibilities were explored for setting down proper balance equations describing mutual interactions of the complex reaction mechanism, creation and variation of the time and space potential differences and resulting transport of the characteristic components. However, here we have to deal with a multicomponent mixture (approximately ten characteristic reaction components) and here the quantitative description of electrokinetic phenomena is still in its infancy. If we accept the irreversible thermodynamics approach with linear flux relations (and accept the local equilibrium assumption), then we shall obtain the relation between potential gradient and concentration changes for a isothermal isobaric one-dimensional system, e.g., in the form [30]

$$-F\,\mathrm{d}\psi/\mathrm{d}z = F(I/\bar{k}) + \sum_j \bar{t}_j^{I} RT\,\mathrm{d}\ln a_j/\mathrm{d}z \qquad (7)$$

where I denotes the electric current, $\bar{t}_j^{I}$ the reduced transport number, and $\bar{k}$ the electrical conductance. The mass flux of the jth component can then be described in the form of the Nernst–Planck equation as

$$N_j = c_j \nabla \mu_j = -g(\bar{t}_j^{I}, c_j) - D_j \nabla c_j + c_j \bar{v}\,, \qquad (8)$$

and used in the proper balance equations for a given experimental system. The values of $\bar{t}_j^{I}$, $\bar{k}$ and the function $g(\bar{t}_j^{I}, c_j)$ have to be fitted experimentally. The work on this is under way. Similar problems appear in the description of the propagation of the nerve signals [31,32].

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