The Belousov–Zhabotinsky Reaction under External Periodic Influence near the SNIPER Bifurcation Point

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Experimental results of an oscillatory reaction of the Belousov–Zhabotinsky type in the system Mn^{2+}–$KBrO_3$–H_2SO_4 – citric acid are depicted. The transition from the steady state to oscillations occurs through the so-called saddle-node infinite period (SNIPER) bifurcation.

Moreover, the dynamic behaviour of this system subjected to external periodic influence has been examined. This was realized by the periodic change in the concentration of $KBrO_3$ in one input solution. Various responses of the system were observed: the synchronization of output oscillations with external forcing, complex periodic oscillations, regions of transient behaviour and chaos. This behaviour has been analyzed by one-dimensional next-period maps, and the Poincaré map for chaos has been constructed.

The appearance of periodic and aperiodic oscillations in chemical systems, particularly in a flow-through continuously stirred tank reactor (CSTR), has recently become a subject of intensive research. Experimental techniques and methods of the time series evaluation of oscillating concentrations are well developed.[1,2] Much research concerning complex periodic and chaotic states has been conducted in regimes in which two or more coupled oscillators interact. Experimental results often lead to similar observations, such as the synchronization of oscillations at a common frequency, amplitude amplification, rhythm splitting or, finally, non-periodicity. Experimental studies of these phenomena have been carried out by Marek and Stuchl,[3] Nakajima and Sawada[4] and Crowley and Field.[5] The mathematical techniques used in analyzing such reacting systems can be found in the work of Ashkenazi and Othmer,[6] Rand and Holmes[7] and Ermentrout and Kopell.[8]

The self-oscillatory system with external periodic forcing may be a model of the interaction of two oscillators. Many interesting phenomena concerning the behaviour of the system, including chaos, can be observed in this case, despite considerable simplifications. An excellent recent review of periodically perturbed chemical systems has been made by Rehmus and Ross.[9] Dolnik *et al.*[10] have described the results of an experiment similar to the one presented here. In their experiment the oscillatory reaction in the CSTR was perturbed by a portion of Br^- ion solution injected periodically. The parameters, i.e. time intervals between the succeeding impulses at which multiple or transient oscillations occur, have been found.

The most persuasive experiments relevant to the BZ reaction have been performed in systems where a change of flow rate results in an alternating sequence of periodic and chaotic states.[11-13]

Our paper contains descriptions and results of investigations in a reaction system in which a sequence of periodic and aperiodic oscillations is obtained which is dependent on the frequency change of the concentration of one input solution. We used Mn^{2+} as the catalyst and citric acid as the organic reagent instead of cerium ions and malonic acid generally used in CSTR investigations. Citric acid and ceric sulfate were used as substrates in the revealing work of Belousov in 1958.[14]

Experimental

Studies were carried out in a 70 cm^3 CSTR thermostatted at 22.5 °C with a mechanical stirrer and a controlled stirring rate; the stirring intensity was 500 r.p.m. Reactant solutions were injected by a two-channel peristaltic pump through two independent inlets provided in the base of the reactor. The flow rate was 0.06 $cm^3\ s^{-1}$ (the residence time in the reactor was about 19 min). The state of the system was followed by measuring the potential of a platinum electrode using a saturated calomel electrode as reference. The platinum electrode potential corresponds to the summary redox potential, for which a decisive part is the $[Mn^{3+}]/[Mn^{2+}]$ couple. Moreover, a bromide ion selective electrode (Radelkis OP-Br-0711P) was used to measure the Br^- concentration changes. These two potentials were rec-

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orded as functions of time on two Radelkis x–t recorders and on an x–y recorder in order to generate two-dimensional phase portraits of the complex behaviour of the system. The Pt electrode recorded oscillations which were of relaxational character, i.e. they consisted of very fast jumps in potential followed by a slower potential decrease. This formed a basis by which to measure the oscillation period. The period of consecutive oscillations was defined as the time interval separating two successive jumps of the potential.

The solutions were prepared using analytical grade reagents from Polskie Odczynniki Chemiczne (Polish Chemical Reagents). Their purity was 99.8 %.

On the basis of preliminary investigations the following input solutions were chosen:

Solution A: $[MnSO_4] = 10^{-2}$ M
$[H_2SO_4] = 2$ M
$[C_6H_8O_7] = 8\times10^{-2}$ M

Group of solutions B: $[KBrO_3]$ from 2×10^{-4} to 4×10^{-2} M

The concentrations of $MnSO_4$, H_2SO_4 and citric acid were kept fixed in all series of measurements. The concentration of $KBrO_3$ in solution B was changed in a stepwise manner, first from higher to lower $[KBrO_3]$ and then from lower to higher concentration. Then the following experiment was performed. Two concentrations of $KBrO_3$ were chosen after suitable investigations:

Solution b_1: $[KBrO_3] = 2.8\times10^{-2}$ M

Solution b_2: $[KBrO_3] = 8\times10^{-3}$ M

Next the system was forced by the automatic change of the supply of solution b_1 for the supply of solution b_2, and vice versa. The frequence of change was kept fixed. The same procedure was repeated for other frequencies of change, so that it decreased stepwise from $2\pi/7200$ s^{-1} to $2\pi/360$ s^{-1}.

For each fixed frequency the experiment was conducted for a sufficiently long time in order to determine which frequency of forcing corresponded to a particular behaviour. Each experimental process lasted for several hours and ended after >100 oscillations. The repetition of experiments gave reproducible results.

Experimental results

In the preliminary part of the experiment a study was made of the dependence of both the period and the amplitude of oscillation on the input concentrations of $KBrO_3$, and the determination of the bifurcation point was investigated. The results are shown in Fig. 1. The transition from the steady state to oscillations occurs at a concentration of ca. 0.25×10^{-2} M $KBrO_3$. With a further increase of $KBrO_3$ concentration the period of oscillations decreases hyperbolically, while the amplitude remains constant. Hysteresis

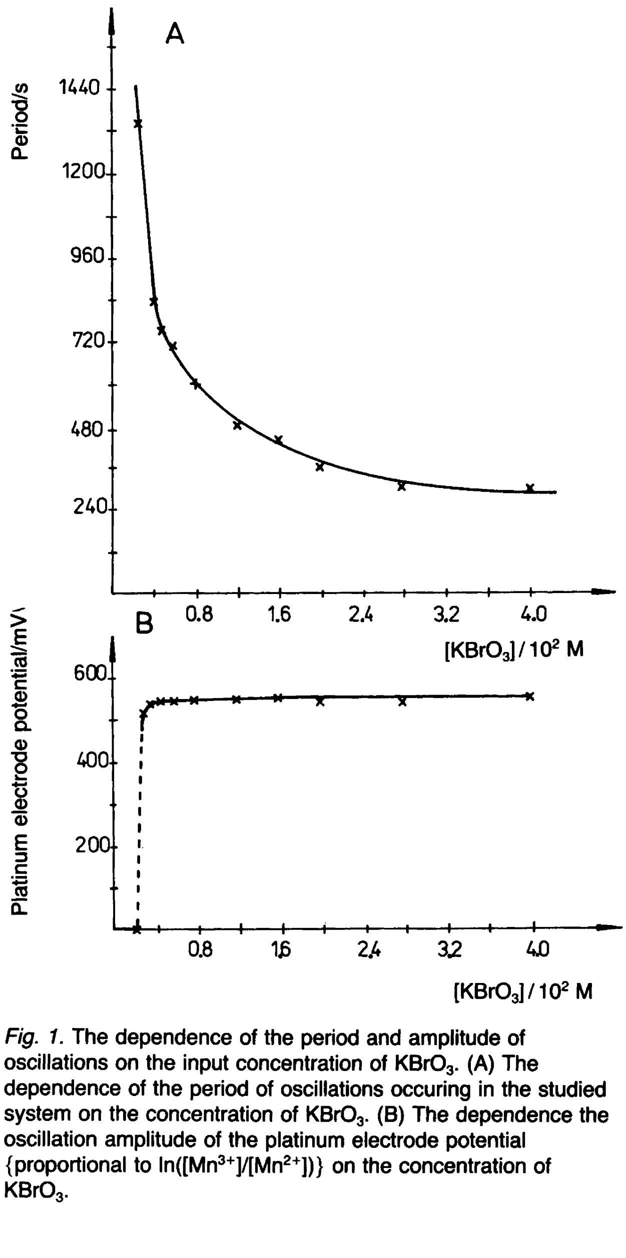


Fig. 1. The dependence of the period and amplitude of oscillations on the input concentration of $KBrO_3$. (A) The dependence of the period of oscillations occuring in the studied system on the concentration of $KBrO_3$. (B) The dependence the oscillation amplitude of the platinum electrode potential {proportional to $\ln([Mn^{3+}]/[Mn^{2+}])$} on the concentration of $KBrO_3$.

does not occur, i.e. the values of amplitudes and periods remain unchanged at a particular measurement point regardless of direction, i.e. from low concentrations to high ones or vice versa. These facts support the hypothesis that so-called saddle-node infinite period (SNIPER)[15] bifurcation occurs. This statement is based on the experimental determination of the structure of the phase portrait of a chemical system in concentration space, developed by Małeko.[16]

Furthermore, the reaction was subjected to periodic forcing. The behaviour of the system differred depending on the value of the forcing frequency. The synchronization of the system with external influences was observed over a wide range of frequencies, in our case the range of frequencies was $> 2\pi/380$ s^{-1} (Fig. 2a). This periodic response to the perturbation had a frequency equal to the frequency of forcing. Such a system is said to be entrained by the

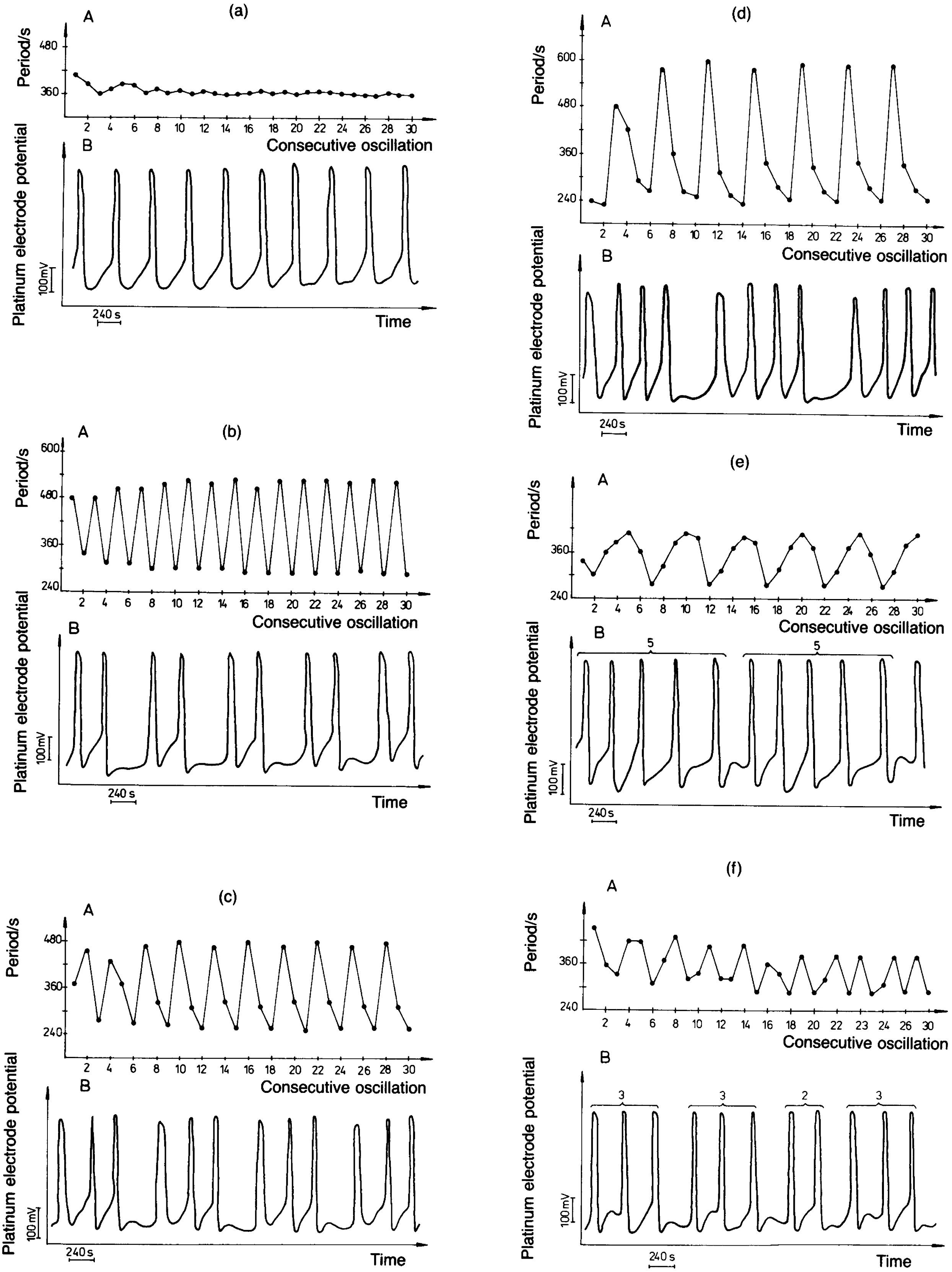
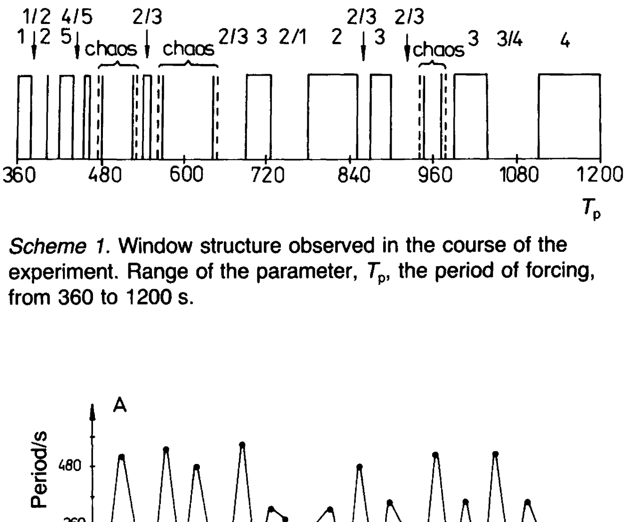


Fig. 2. Various responses of the investigated system to external forcing: (a) entrainment at frequency $2\pi/360\ s^{-1}$, (b) biperiodicity at frequency $2\pi/840\ s^{-1}$, (c) triperiodic oscillations at frequency $2\pi/1020\ s^{-1}$, (d) quadriperiodic oscillations at frequency $2\pi/1440\ s^{-1}$, (e) quinteperiodic oscillations at frequency $2\pi/440\ s^{-1}$, (f) split entrainment band (2- and 3-periodic) at frequency $2\pi/540\ s^{-1}$. (A) Period values of the various oscillations. (B) The fragment of recorded oscillations of the Pt electrode.

perturbation. It is known[9] that if the perturbation has frequency ω_p and if the unperturbed system asympotically approaches a limit cycle with frequency ω_0, then an entrainment band is the region where the response to the perturbation is periodic with a frequency ω, and ω_p is always some integral multiple of ω ($\omega_p = n \times \omega$). In our system $\omega_p = \omega$ rigorously.

Moreover, other classes of interesting behaviour were observed. There are regions of complex periodic oscillations: bi-, tri-, quadri- and quinteperiodic (Figs. 2b–2e). Between them, regions of split entrainment bands occur which resemble an overlapping of complex periodic oscillations; e.g. in Fig. 2f a biperiodic pattern with a triperiodic pattern designed as 2/3 for the frequency $2\pi/540\ s^{-1}$ is presented. There are also other relations *m*/*n* of split entrainment regions. These regions occur between suitable *m*- and *n*-periodic oscillations (Scheme 1).

Chaos was also observed in the investigated system at certain frequencies (e.g. $2\pi/640\ s^{-1}$). A period doubling set of bifurcations was not observed as, for example, in the chemical model reported by Tomita.[17] In frequency ranges in which chaotic behaviour occurs, the periods of separate oscillations and their shapes change, but the amplitudes of



Scheme 1. Window structure observed in the course of the experiment. Range of the parameter, T_p, the period of forcing, from 360 to 1200 s.

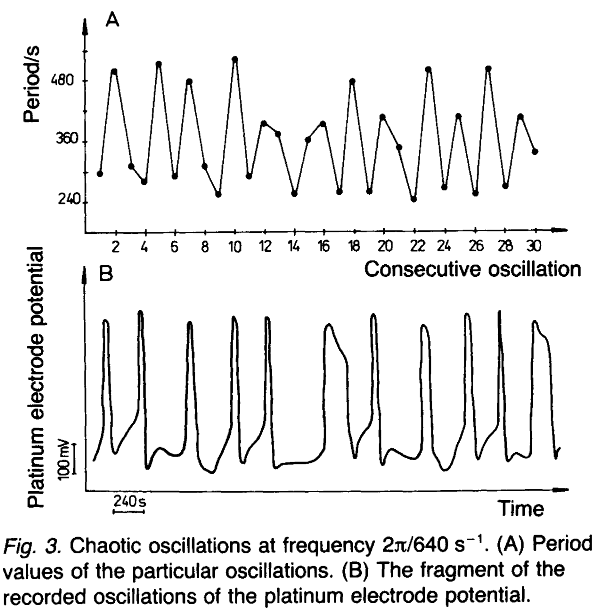


Fig. 3. Chaotic oscillations at frequency $2\pi/640\ s^{-1}$. (A) Period values of the particular oscillations. (B) The fragment of the recorded oscillations of the platinum electrode potential.

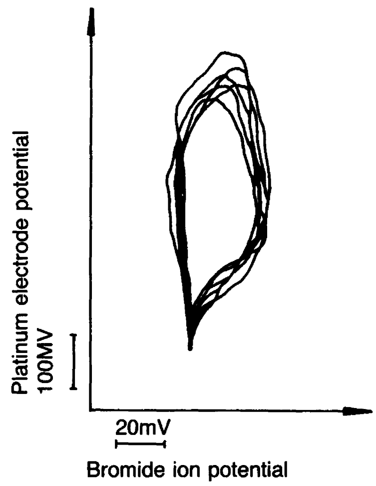


Fig. 4. Phase portrait obtained in the case of chaotic oscillations (frequency $2\pi/640\ s^{-1}$).

all oscillations are constant (Fig. 3). The phase portrait in this case is shown in Fig. 4. In the course of the measurements a phase-portrait broadening, typical of chaos, is observed (succeeding recorded loops do not coincide). Fig. 4 presents only a few such loops for clarity of presentation.

Investigations of the mutual position of subregions of the system with different dynamic behaviour have been made. These subregions form the so-called window structure in ω_p-space shown in Scheme 1. The regions of regular simple or complex periodic oscillations are separated by split entrainment bands, and each chaotic region is preceded by regions of increasing *n*-periodicity.

One-dimensional return maps

For a more detailed analysis of periodic, complex periodic and chaotic behaviour in the investigated system one-dimensional return map methods have been used. Next-time period maps were constructed for *n*-periodic complex oscillations, whereas for chaos a one-dimensional Poincaré map was, in addition, applied.

The dependence of the consecutive current period T_{n+1} on the preceding period T_n [eqn. (1)] is obtained from

$$T_{n+1} = f(T_n) \tag{1}$$

measurements of the time intervals separating two successive jumps of the Pt electrode potential.

Examples of these maps for our experiment are shown in Fig. 5. In the case of periodic output it is interesting to note that the mapping corresponds to the 1-periodic cycle, Fig. 5a. Namely, it tends very rapidly towards the fixed point. When the *n*-periodicity of oscillations is increasing, more fixed points consequently appear. The groups of points, as a whole, depict the shape of the supposed transfer function, eqn. (1). An important result is that the shapes of these functions are different for oscillations with

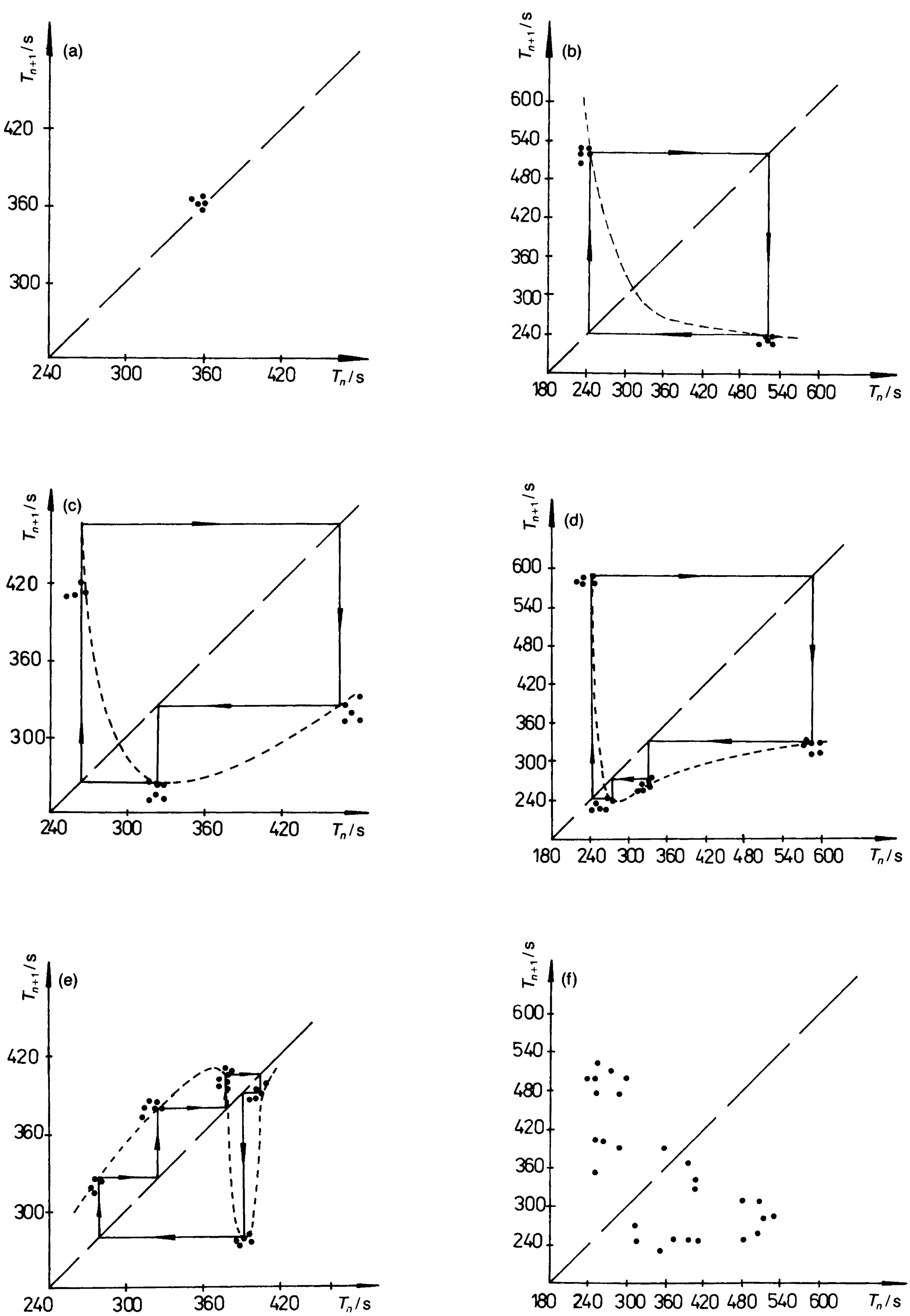


Fig. 5. The next-period maps: (a) for periodic oscillations at frequency $2\pi/360\ s^{-1}$, (b) for biperiodic oscillations at frequency $2\pi/840\ s^{-1}$, (c) for triperiodic oscillations at frequency $2\pi/1020\ s^{-1}$, (d) for quadriperiodic oscillations at frequency $2\pi/1440\ s^{-1}$, (e) for quinteperiodic oscillations at frequency $2\pi/440\ s^{-1}$, (f) for chaotic oscillations at frequency $2\pi/640\ s^{-1}$.

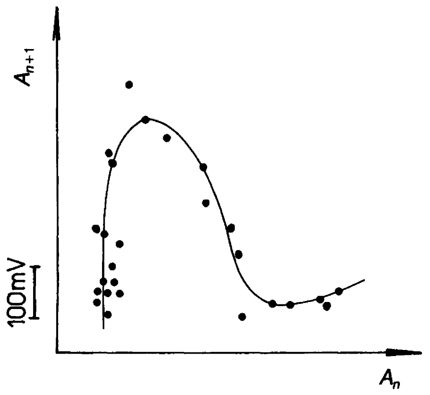


Fig. 6. The one-dimensional Poincaré map for chaotic oscillations at frequency $2\pi/640\ s^{-1}$.

different n-periodicities. These functions are presented in Figs. 5b–e as dashed lines. The solid lines with arrows denote the n-cycle output. A similarity of the transfer functions in the cases of 2-, 3- and 4-periodic oscillations (Figs. 5c and d) may be explained by the neighbouring forcing frequencies (Scheme 1).

In the case of chaos (Figs. 5f) the successive points do not form a single-valued transfer function (as in Figs. 5b–e). That is, a period T_n may be followed by periods corresponding to a number of T_{n+1} values. A similar piecewise linear placing of points on the T_n–T_{n+1} surface suggests that in another transformation a continuous relationship would be obtained. To test this, a one-dimensional Poincaré map, with a time interval equal to the period of forcing, was applied according to eqn. (2), in which X is the potential

$$A_{n+1} = F(A_n) = X(t_n + 2\pi/\omega_p) \tag{2}$$

measured on the platinum electrode, ω_p is the frequency of forcing, and $t_n = t_0 + 2\pi n/\omega_p$, where t_0 is the initial point.

The shape of the curve obtained (Fig. 6) is similar to the frequently described cubic one-dimensional map.[18] It supports the evidence that the oscillatory process in the applied experimental conditions has a chaotic character. The points that lie off this line are a result of spontaneous fluctuations of the studied chemical system.

Conclusions

For the BZ reaction in the system containing citric acid we have examined the character of the bifurcation at the transition from the stable steady state to the oscillatory regime. The influence of external periodic forcing, realized by a periodic change of one input solution, on the chemical oscillator have been studied. Qualitatively different responses, beginning with the periodic, through n-periodic oscillations and more complicated split entrainment bands, up to extremely complex dynamics of the system (chaos), have been obtained.

Moreover, the next-period maps and one-dimensional Poincaré map have been constructed in order to distinguish the complex periodic oscillations from chaos. The one-dimensional Poincaré map proves that chaotic output was obtained in the investigated system.

Further investigations dealing with the oscillatory processes by mathematical modelling and power-spectrum analysis are in course.

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