A Transition Sequence of Complex Oscillations in a Chemical Oscillation Model Showing Chaos

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A three-variable model system exhibiting complex oscillations was analyzed. Our analysis reveals a bifurcation structure of complex oscillations including chaotic oscillations. The bifurcation structure reproduces well the transition sequences of oscillatory states observed in the experiments of the Belousov–Zhabotinskii reaction and the chlorite oscillators. The transition sequence to chaotic oscillations in our model system shows period-doubling sequences. When the number F is defined as a ratio of the number of large amplitude to the total number of oscillations per period in the complex oscillation, the number constitutes a monotonous, stepwise-increasing function of a control parameter. The sequence of the complex oscillations is described well by the Farey arithmetic. Also, the average flux of reaction was found to change abruptly at the bifurcation points of the complex oscillations.

In recent years much attention has been paid on the complex oscillations and the chaotic oscillations in the oscillating chemical reactions, and numerous experimental and theoretical studies have been made.[1–4] The complex oscillations were first investigated by Belousov and Zhabotinskii,[5] and Hudson et al. reexamined in detail the Belousov–Zhabotinskii (BZ) reaction in a continuous flow reactor and confirmed that the complex oscillations continued steadily.[6,7] Their experiments exhibited various types of complex oscillations and chaotic oscillations depending on the flow rate of the reactant solutions. Similar phenomena have been also observed in various chlorite oscillators.[8,9] Every complex oscillation reported hitherto is composed of a combination of small and large amplitude oscillations per period. Theoretical investigations on the appearance of complex oscillations have been also performed. Especially, studies on the modified Oregonator[10] may be the most representative.[11–14]

In a previous paper we proposed a simple model to explain chemical oscillations.[15] Moreover, with some modification of the original model system, we constituted a new model system showing some complex oscillations consisting of concatenating small and large amplitude oscillations and explained a mechanism for occurrence of such complex oscillations.[16]

Recently, transition sequences of complex oscillations have been observed in careful and detailed experiments.[17–19] To understand these transition sequences of periodic states, theoretical studies have been carried out by means of one-dimensional maps[20–22] and model systems.[23,24] Many experimental and theoretical efforts have been made to establish the theory of bifurcation structures in oscillating chemical reactions, but still now we can say that bifurcation structures including chaotic oscillations have not been adequately understood.

In the present paper we report a bifurcation structure of complex oscillations including chaotic oscillations by analyzing our simple model with three variables. The model exhibits a quite similar transition sequence of the complex oscillations observed in the BZ reaction[6,7,17–19] and the chlorite oscillators.[8,9] All the complex oscillations appear in the region between the singly small amplitude oscillation and the singly large amplitude oscillation. Mode locking is observed in the transition sequence of complex oscillations. And combined complex oscillations and chaotic oscillations were observed between two stable complex oscillations. The transition sequence from a complex to the chaotic oscillation was period doubling. A complex oscillation becomes unstable with an increase in a control parameter value and a 2-cycle period oscillation appears and then, when the parameter increases, 2^2, 2^3,…, 2^k-cycle oscillations appear and finally an aperiodic state (chaotic oscillation) is followed. When the control parameter increases further, the aperiodic state becomes unstable and a 3-cycle oscillations appears. This sequence was predicted by Li and Yorke.[25]

When an oscillatory state is characterized by a number F, the ratio of the number of large amplitude peaks to the total number of peaks per period, F is a monotonous stepwise-increasing function of a control parameter and forms a staircase similar to the so-called "devil's staircase".[26] The transition sequence of complex oscillations is described well by Farey series.[27]

In order to consider meanings of the staircase structure, the average flux of reaction of each oscillatory state was calculated and a distinct relationship between the oscillatory state and the average flux of reaction was found.

The main purpose of this paper is to show the global feature of the bifurcation structure in our model. Details of respective cases will appear somewhere.

The Model

In a previous paper, we proposed a two-variable chemical system exhibiting temporal oscillations.[15] In a succeeding paper of it, a three-variable model system exhibiting complex oscillations was derived by some modification of the original system and its behavior was analyzed.[16] In this paper, the modified system was investigated in order to make clear the bifurcation structure of the complex oscillations including chaotic oscillations. The system is consisting of the following chemical reactions;[16]

$$P + Z \xrightarrow{k_1} E + Z, \quad (R1)$$

$$E + X \xrightarrow{k_2} R + X, \quad (R2)$$

$$A + 2X + E \underset{k_4}{\overset{k_3}{\rightleftharpoons}} 3X + E, \quad (R3)$$

$$B + X \underset{k_6}{\overset{k_5}{\rightleftharpoons}} C, \quad (R4)$$

$$Q \xrightarrow{k_7} Z, \quad (R5)$$

$$Z + X \xrightarrow{k_8} D + X, \quad (R6)$$

where A, B, P, and Q are reactants, C, D, and R are products and E, X, and Z, are intermediates. In the model the concentrations of all the reactants and the products are assumed to be constant, keeping the system effectively far from equilibrium. For simplicity, the symbols for the chemical species are used also to denote their concentrations. The differential equations describing the dynamic behavior of this model are given by applying the law of mass action to Reactions (R1)—(R6);

$$\frac{dE}{dt} = k_1PZ - k_2EX, \quad (1)$$

$$\frac{dX}{dt} = k_3AEX^2 - k_4EX^3 - k_5BX + k_6C, \quad (2)$$

$$\frac{dZ}{dt} = k_7Q - k_8XZ. \quad (3)$$

k_i's denote forward or backward rate constants for Reactions (R1)—(R6). The numerical values of k_1 through k_8, A, B, C, and Q are given as follows: $k_1=1.0$, $k_2=5.0$, $k_3=100.0$, $k_4=50.0$, $k_5=10.0$, $k_6=1.0$, $k_7=0.1$, $k_8=0.4$, $A=1.3$, $B=5.0$, $C=5.3$, and $Q=1.0$. Equations 1—3 were calculated by the double-precision Runge–Kutta–Gill method with a digital computer. P is set as a control parameter and every calculation was carried out by assigning a proper value of P.

Bifurcation Structures of Complex Oscillations

According to the results of linearized stability analysis, the steady state of the present chemical system is unstable in the region, $1.034<P<14.21$. The differential equations (Eqs. 1—3) were solved numerically to confirm the occurrence of sustained oscillations at these unstable steady states. Complex oscillations formed from combinations of small and large amplitude oscillations appear, as an example is illustrated in Fig. 1. A mechanism for the occurrence of the complex oscillations has been proposed in the preceding paper.[16] Figure 1(a) shows the temporal change of the intermediate X at $P=1.13$. This complex oscillations is formed by concatenating one large amplitude and four small amplitude oscillations per period. Figure 1(b) shows a three-dimensional view of this complex oscillation. A common feature of the complex oscillations observed in our system is that they consist of periodic repetitions of a basic pattern of a large amplitude oscillation followed by some small amplitude oscillations. Therefore, these typical complex oscillations can be characterized by a number n, the total number of peaks per period. The notation $\pi(n)$ is used hereafter to describe the complex oscillation formed from the combination of one large peak and $(n-1)$ small peaks per period. The oscillation shown in Fig. 1 is $\pi(5)$.

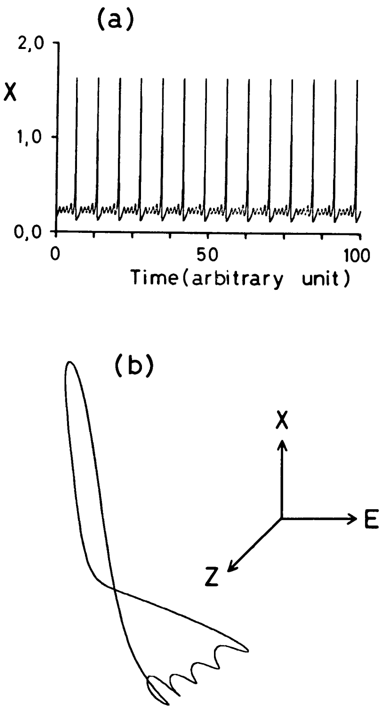

Fig. 1. A behavior of the complex oscillation $\pi(5)$ in our model. (a) Temporal change X vs. time, (b) three dimensional view in the E-X-Z space. $P=1.13$.

Figure 2 shows the relationship between the number n and the parameter P. With an increase in the value of P, the number of small peaks per period decreases by one. Here, $\pi(1)$ represents a single, large amplitude oscillation. It is noteworthy that the mode locking exerts in these oscillations and the number n is a

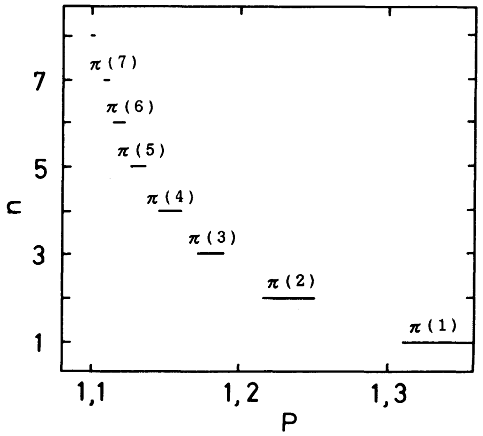

Fig. 2. A mode locking structure of complex oscillations. Relationship between the control parameter P and the number n which characterizes the states of complex oscillations.

staircase-like function of P. The oscillation region of $\pi(n)$ and the transition region between $\pi(n+1)$ and $\pi(n)$ become larger for the smaller number of n.

The property of mode locking has been noticed also in the BZ reaction[17–19] and a one-dimensional map has been utilized to describe the sequence of oscillatory states in the BZ reaction.[20] The mode locking behaviors have been occasionally observed in nonlinear systems having 2-torus attractor,[28–34] even though we do not confirm the existence of two distinct oscillators in these systems.

More complex oscillations appear in the parameter range between $\pi(n)$ and $\pi(n-1)$. They are a periodic oscillation formed from the combination of $\pi(n)$ and $\pi(n-1)$ per period and a chaotic oscillation. Typical examples are shown in Fig. 3. Figure 3(a) shows a periodic oscillation where $\pi(2)$ and $\pi(3)$ appear alternately. Hereafter we call this type oscillation as a combined complex oscillation and designate as $\pi(3)\pi(2)$ for an example. Figure 3(b) shows a more complicated periodic oscillation consisting of a 3-cycle oscillation of $\pi(2)$ and a 1-cycle oscillation of $\pi(3)$ per period. The general notation of these combined complex oscillations is $[\pi(n)]^k[\pi(n-1)]^m$; a periodic oscillation formed from the combination of k-cycle oscillation of $\pi(n)$ and m-cycle oscillation of $\pi(n-1)$. The combined complex oscillation shown in Fig. 3(b) is $[\pi(3)][\pi(2)]^3$. Noteworthily, almost all the combined complex oscillations between the regions of $\pi(n)$ and $\pi(n-1)$ consist of the combination of $\pi(n)$ and $\pi(n-1)$. Moreover, a chaotic oscillation observed in this region consists of aperiodic repetitions of $\pi(n)$ and $\pi(n-1)$, as Fig. 3(c) illustrates. However, there are some exceptional cases where the chaotic oscillations in the region between $\pi(n)$ and $\pi(n-1)$ consist of not only $\pi(n)$ and $\pi(n-1)$ but also $\pi(k)$ with k except for n and $n-1$. An example is shown in Fig. 3(d). On a chaotic oscillation we will explain in detail the bifurcation

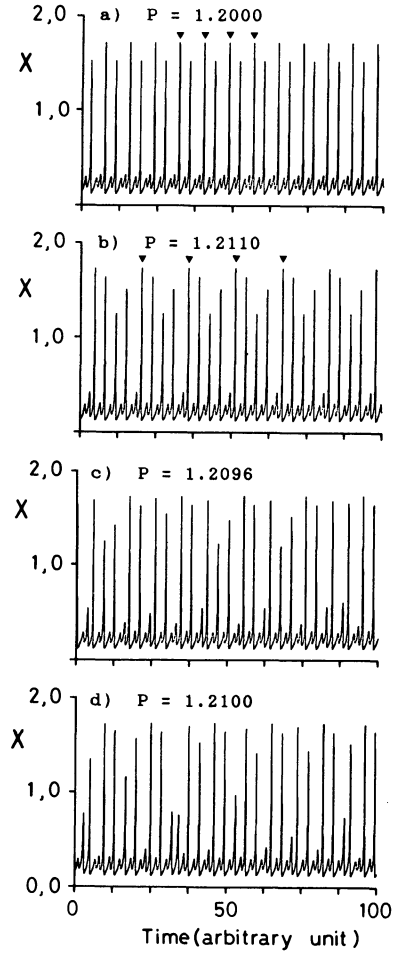

Fig. 3. The combined complex oscillations and the chaotic oscillations. (a) P=1.20: $\pi(3)\pi(2)$, (b) P=1.211: $[\pi(3)][\pi(2)]^3$, (c) P=1.2096 and (d) P=1.21: chaos. Each mark above the oscillations shows the period.

structure in the following papers.

In order to explain the transition sequence including combined complex oscillations and chaotic oscillations, we put a suitable rational between n and $n-1$ to a periodic oscillation of $[\pi(n)]^k[\pi(n-1)]^m$ and plot against P on the n–P two-dimensional phase diagram, as seen in Fig. 4. The mode locking is observed again. The combined complex oscillation of $\pi(n)\pi(n-1)$ occupies a larger region between $\pi(n)$ and $\pi(n-1)$ than other combined complex oscillations of $[\pi(n)]^k[\pi(n-1)]^m$ $(k\neq m)$. Every chaotic oscillation takes place in a very limited region. Figure 5 shows an outline of the transition sequence of oscillatory states between $\pi(2)$ and $\pi(1)$. Figure 6 shows the examples of corresponding oscillation states. The oscillation $\pi(2)$ (a) bifurcates successively to $[\pi(2)]^2$ (b), $[\pi(2)]^4$ (c), $[\pi(2)]^8$ (d),$\cdots$, resulting in an aperiodic oscillation (e) formed from $\pi(2)$, as P increases. When P increased beyond over the chaotic region, a 3-cycle oscillation $[\pi(2)]^3$ (f) and a different type chaotic oscillation (g) were found to appear without any period-doubling sequence. The

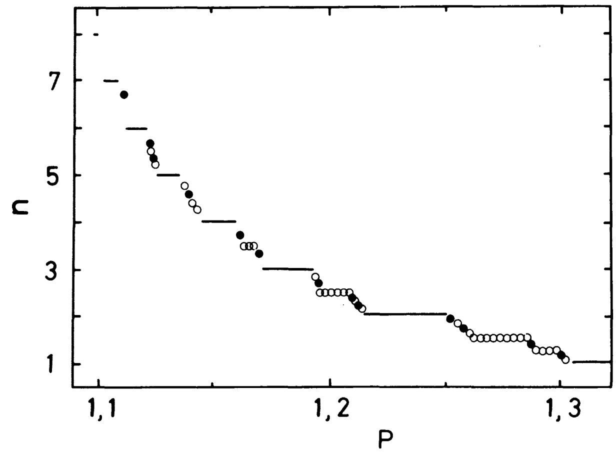

Fig. 4. Relationship between the control parameter P and oscillatory states. Symbols; (—) complex oscillation $\pi(n)$, (○) combined complex oscillation $[\pi(n)]^k[\pi(n-1)]^m$, (●) chaotic oscillation.

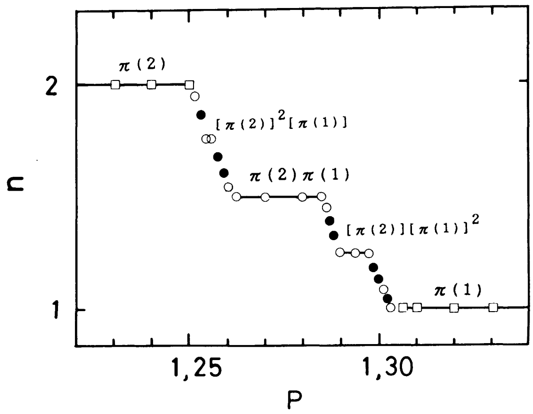

Fig. 5. A sequence of oscillatory states between $\pi(2)$ and $\pi(1)$ by varying the control parameter P. Symbols; (□) complex oscillation $\pi(n)$, (○) combined complex oscillation $[\pi(n)]^k[\pi(n-1)]^m$, (●) chaotic oscillation.

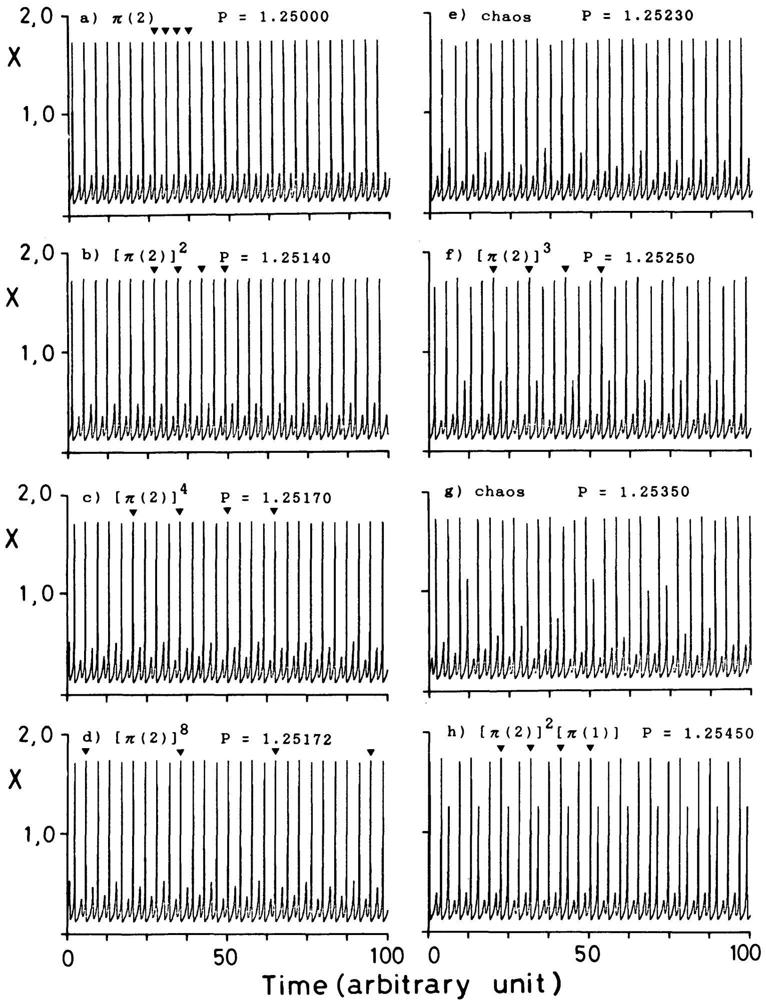

Fig. 6. A transition sequence of oscillations between $\pi(2)$ and $[\pi(2)]^2[\pi(1)]$. Each mark above the oscillations shows the period.

latter chaotic oscillation consists of a combination of $\pi(2)$ and $\pi(1)$. Then, the system leads a combined complex oscillation $[\pi(2)]^2[\pi(1)]$ (h) formed by concatenating $\pi(2)$ and $\pi(1)$, which shows period-doubling as an increase in P till it becomes unstable. After repetitions of these processes, $\pi(2)\pi(1)$ and finally $\pi(1)$ occur.

The transition sequence from $\pi(n)$ to $\pi(n-1)$ with an increasing P can be summarized as follows:

$$\pi(n) \to [\pi(n)]^2 \to [\pi(n)]^4 \to\to \text{chaos} \to [\pi(n)]^3 \to \text{chaos} \to\to\to [\pi(n)]^k[\pi(n-1)]^m\,(k>m) \to\to \text{chaos} \to \to \pi(n)\pi(n-1) \to\to \text{chaos} \to\to [\pi(n)]^k[\pi(n-1)]^m\,(k<m) \to\to \text{chaos} \to [\pi(n-1)]^3 \to\to \text{chaos} \to [\pi(n-1)]^4 \to [\pi(n-1)]^2 \to \pi(n-1),$$

where $[\pi(n)]^k$ is a k-cycle oscillation of $\pi(n)$.

According to Maselko and Swinney,[18,19] we define a following number F which characterizes each complex oscillation;

$$F = L/(L + S),$$

where S and L are respectively the numbers of small and large amplitude oscillations per period. For examples, the complex oscillation $\pi(n)$ has the number of $F=1/n$ and the combined complex oscillation $\pi(n)\pi(n-1)$ has $F=2/(2n-1)$. Of course, some of the different oscillations have the same value of F; e.g. both $\pi(2)$ and $[\pi(2)]^2$ have $F=1/2$.

Figure 7 shows the relationship between F and P, where F forms a staircase as a function of P. F equals 1/2 in a discrete wide range of P. The regions having the values of 1/3, 2/3, 1/4, and 3/4 are also clearly distinguishable. $F=1/2$ represents a series of periodic states formed from $\pi(2)^n$, where $n=1, 2, 4, 8, \cdots\cdots 5, 3$ (Sarkovskii sequence).[36] Similarly, 1/3, 2/3, and 1/4, respectively show $\pi(3)^n$, $[\pi(2)\pi(1)]^n$, and $\pi(4)^n$, where $n=1, 2, 4, 8, \cdots 5, 3$. Aperiodic states (chaotic oscillations) are thus included in this figure, but the case shown in Fig. 6(g) is difficult to define its value of F and to show in this figure. This staircase is similar

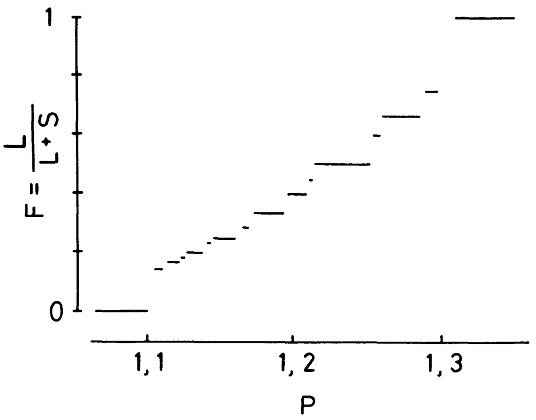

Fig. 7. A staircase behavior of the number F vs. P.

to the "devil's staircase".[26] The devil's staircase has as infinite self-similar staircase structure and is a representative example of fractal, which has been often observed in nonlinear systems. For examples, the one-dimensional Ising model[31] and the sine circle map[32,33] exhibit the devil's staircase.

Recently, Maselko and Swinney have found a similar staircase in the BZ reaction.[18,19] They studied two types of sequences, a complex oscillation composed of two basic patterns and that of three basic patterns. The former sequence is in conformity with the experimental results by Hudson et al. These sequences could be well reproduced in our model.

It has been noticed that the ordering of the number F is related to the Farey series,[18,19,30] when the system has the staircase structure. The Farey series is given by the following procedure; starting with two fractions, 0/1 and 1/1, we get a new fraction according to the following equation.

$$a/b \oplus c/d = (a + c)/(b + d).$$

The first Farey series is 0/1, 1/1, the second is 0/1, 1/2, 1/1, the third is 0/1, 1/3, 1/2, 2/3, 1/1, and so forth. The series of F in Fig. 7 is in a good agreement with the Farey series. It is noteworthy that the complex oscillation having a smaller denominator in the Farey number occupies the wider region. 0/1 and 1/1 represent the single oscillations with a smaller and a larger amplitude, respectively.

Relationship between Oscillatory States and the Average Flux of Reaction

As described above, the transition sequence of complex oscillations in the BZ reaction could be simulated by means of our system. The transition behavior suggests us that there should exist some quantities that change discontinuously at the transition, like entropy or heat capacity in the ordinary phase transition of first or second order. Although it is not yet confirmed that such a quantity exists in the dynamic transition point, we tried to calculate the flux of reaction and examine its relationship to the oscillation states, because the system concerned is a non-equilibrium state far from equilibria and the flux of reaction is one of the essential quantities that characterize the dynamic state of system and determine the entropy production rate. In the case of the one-dimensional Ising model, it has been proved that the staircase structure appears under the conditions that the total energy of the system should be minimized at a given magnetization.[31] Thus, we intend to find a useful quantity like the total energy in the Ising model to explain the staircase structure. Here, we examine the relation between each oscillatory state and its flux of reaction. The average flux of reaction was determined from the integrated flux of the reaction for a

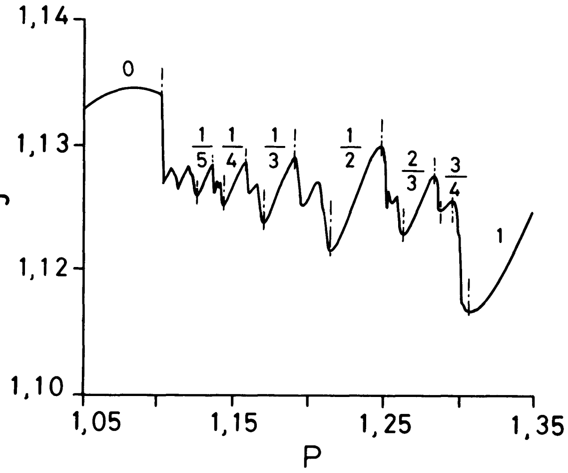

Fig. 8. Relationship between P and average flux of reaction. The values of F for the representative states are given in the figure.

sufficiently long period divided by the integration time.

Figure 8 shows the relationship between P and J, where J is the consuming rate of P ($J=k_1PZ$). Compared with Fig. 7, the average flux J increases monotonously in the region of a (combined) complex oscillation and start to decrease where the period-doubling sequence begins to occur. That is, the inflection point from an increase to a decrease in J coincides perfectly with the starting point of changing from a complex oscillation toward the next one. In some cases where a periodic oscillation changes to a chaotic oscillation without showing any period-doubling sequence, the changes in J are drastic. The value of J would exhibit the same tendency as the value of entropy production rate.[37] Further investigations are needed.

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