Behavior of Trajectory with Stable and Unstable Limit Cycles in the Oregonator Model for the Belousov-Zhabotinskii Reaction

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Computer simulations and a theoretical analysis of the Oregonator model of the Belousov-Zhabotinskii reaction are made based on Tyson's equation. The behavior of the amplitudes of the unstable limit cycle near the transition point, p_c, can be explained theoretically fairly well by the Landau theory. The global behavior of one stable limit cycle and one unstable limit cycle is examined by means of simulations. The existence of a triple point at which three different global states coexist has been suggested.

Field and Noyes[1] have proposed a simple model (Oregonator model) for the kinetics of the Belousov-Zhabotinskii (B-Z) reaction. Tyson[2] presented this model as follows,

$$\begin{aligned} \varepsilon \frac{dx}{dt} &= x + y - qx^2 - xy, \\ \frac{dy}{dt} &= -y + fz - xy, \\ p\frac{dz}{dt} &= x - z, \end{aligned} \tag{1}$$

where t, x, y, and z are the dimensionless variables corresponding to the time and the three concentrations $[HBrO_2]$, $[Br^-]$, and $[Ce^{4+}]$ respectively, and where ε, f, p, and q are the dimensionless parameters to be decided from the rate constants of the elementary reactions, the concentration of $BrCH(COOH)_2$, *etc.* The stiffly coupled approximation $dx/dt=0$ has been introduced into Eq. 1.[1,2] The meaning of this approximation has been discussed in detail by Field and Noyes[1] and by Tyson.[2] Simply speaking, this approximation is obtained by postulating that bromous acid is always present in a steady state concentration as determined by the concentration of bromide ions. Under the stiffly coupled approximation, we get:

$$\begin{aligned} \dot{\bar{y}} &= -\delta\bar{y} + f\bar{z} - (\gamma+\bar{y})X(\bar{y}), \\ \dot{\bar{z}} &= r\{X(\bar{y})-\bar{z}\}, \quad r = \frac{1}{p}, \end{aligned} \tag{2}$$

where $\bar{y}$ and $\bar{z}$ are the deviations of y and z from the steady state values y_0 and z_0, respectively; where the dot shows the time differentiation, and where

$$X(\bar{y}) = \{-(\alpha+\bar{y})+\sqrt{(\alpha+\bar{y})^2-4q\beta\bar{y}}\}(2q)^{-1}.$$

The detailed derivation of Eq. 2 and the definition of the constants, α, β, γ, and δ, may be seen in Ref. 3. For the sake of simplicity, we call this model (Eq. 2) the simple Oregonator model.

In a previous paper[3] we made computer simulations of Eq. 2. These simulations confirmed the coexistence of an unstable limit cycle and a stable limit cycle. Figure 1 shows a typical example of the coexistence state of the two limit cycles around a stable steady state. In the figure, the dot-dash-line denotes the trajectory. The solid line shows the stable limit cycle, and the dotted line, the unstable limit cycle, as estimated from the simulations. The steady state (y_0, z_0) is represented by the symbol "a." In order to analyze the behavior of the simple Oregonator model theoretically, we must define two quantities: the amplitude, A, of a trajectory and the amplitude-expansion rate, F. The amplitude, A, of a trajectory is defined by the distance between the steady state, "a," and the point at which the trajectory intersects the $z=z_0$ line. The amplitude-expansion rate, F, is defined by the time differentiation of the square of the amplitude, A:

$$\frac{dA^2}{dt} = F.$$

In numerical simulations, the dA^2/dt quantity is determined by $\Delta A^2/\Delta t$, where ΔA^2 and Δt are, respectively, the differences in the squares of the amplitude, A^2, and the time, t, over one turn of a trajectory. The points at which an unstable limit cycle and a stable one intersect the $z=z_0$ line are denoted by the symbols "b"

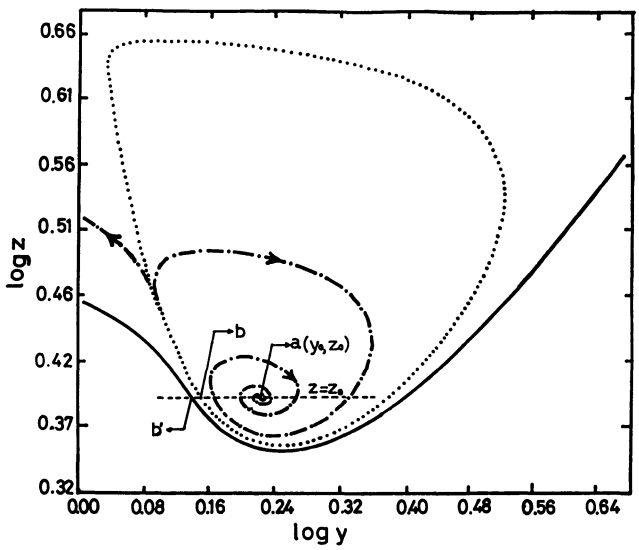

Fig. 1. Phase plane plot of $\log z$ *vs.* $\log y$ obtained numerical integrations of Eq. 1 under $dx/dt=0$ for $q=0.006$, $f=2.350$, and $p=2.0$ ($p_c=90.24$).
……: Unstable limit cycle, ——: stable limit cycle, -·-·-: trajectory, ------: $z=z_0$, a: steady state, ab: A_u (amplitude of unstable limit cycle), ab′: A_s (amplitude of stable limit cycle).

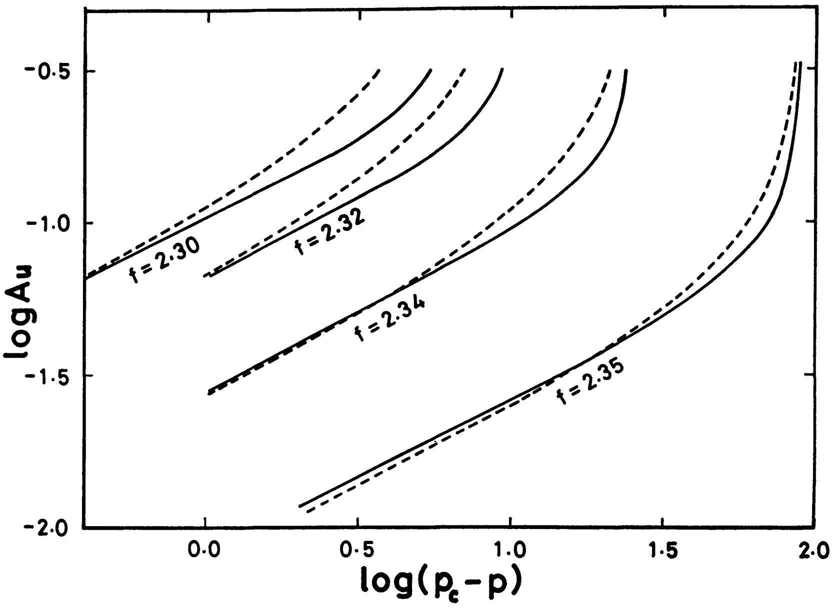

Fig. 2. Log-log plots of A_u *vs.* (p_c-p) for $q=0.006$.
——: Plots of data from computer simulations, ------: theoretical curve from Eq. 18.

and "b′" respectively, as is shown in Fig. 1. We define the A_u and A_s amplitudes (the amplitudes of an unstable limit cycle and a stable-limit one) by the ab and ab′ distances, respectively.

In this paper the behavior of the trajectory and the amplitudes of two kinds of limit cycles are examined for various values of the p and f parameters by means of computer simulations. The changes in the amplitudes of the two kinds of limit cycles are obtained numerically. A quantitative explanation of these changes is made by the use of the Landau theory.[4]

Behavior of an Unstable Limit Cycle near p_c and a Perturbational Approach

Figure 2 shows the log-log plots of the amplitude, A_u, of the unstable limit cycle against (p_c-p). The solid lines represent the results from computer simulations. We will examine, on the basis of the Landau theory, how the behavior of A_u can be explained theoretically. The Landau theory elucidates the transition from a laminar flow to a turbulent one and may be represented as follows:[4]

$$\frac{dA^2}{dt} = F = \gamma_2 A^2 + \gamma_4 A^4 + \cdots. \tag{3}$$

This approach (Landau theory) is a kind of perturbation method. We will show that the behavior of the unstable limit cycle near the transition point p_c can be explained fairly well by means of Landau's equation (Eq. 3).

We determine two coefficients, γ_2 and γ_4, in Eq. 3 by the use of perturbation method. In deriving the nonlinear terms in Eq. 2, which we represent as N_y and N_z, we use the approximation $q=0$, because the q parameter is very small in a real system, of the order of 10^{-6}, as estimated by Field and Noyes.[1] Then, Eq. 2 can be presented as follows:

$$\dot{\bar{y}} = r_c\bar{y} + f\bar{z} + N_y, \qquad \dot{\bar{z}} = ra_1\bar{y} - r\bar{z} + N_z, \tag{4}$$

where the nonlinear terms, N_y and N_z, are given by:

$$N_y = -(b_1\bar{y}^2 + b_2\bar{y}^3 + \cdots),$$
$$N_z = r(a_2\bar{y}^2 + a_3\bar{y}^3 + \cdots), \tag{5}$$
$$a_n = \frac{\beta}{(-\alpha)^n},\ b_n = -\frac{2+r_c}{(-\alpha)^n}\quad (n=1,2,\cdots),$$

and where the constant, r_c, is the boundary value defined by:

$$r_c = \frac{1}{p_c} = \frac{\beta\gamma}{\alpha} - \delta.^{2,3)}$$

The linear approximation ($N_y=0$, $N_z=0$) of Eq. 4 gives two solutions, y_l and z_l (complexes), of these forms:

$$y_l = A_y\exp(\lambda t),\ z_l = A_z\exp(\lambda t), \tag{6}$$

where the eigenvalue, λ, is:

$$\lambda = \lambda_0 + i\omega,$$
$$\lambda_0 = -\frac{1}{2}(r-r_c), \tag{7}$$
$$\omega \simeq -r\sqrt{(r_c+a_1f)},\ (r \simeq r_c).$$

We seek this solution:

$$\bar{y} = \mathrm{Re}(y_l+y_n),\ \bar{z} = \mathrm{Re}(z_l+z_n), \tag{8}$$

where Re denotes the real part. The contributions to y_n and z_n from nonlinear terms are determined to be of these forms:

$$y_n = B_y\exp(2i\,\omega_c\,t) + C_y,$$
$$z_n = B_z\exp(2i\,\omega_c\,t) + C_z, \tag{9}$$

where ω_c is ω at $p=p_c$. The constants, B_y and C_y, are determined to be exact up to the A_y^2 order, whereas B_z and C_z are exact to the A_z^2 order. Putting Eq. 8 into Eq. 4, we get:

$$B_y = -\frac{1}{6}cA_y^2,\ C_y = \frac{1}{2}c|A_y|^2, \tag{10}$$

where:

$$c = \frac{b_1 - a_2 f}{r_c + a_1 f}.$$

The amplitude, A, is given by:

$$A = y_l + y_n \simeq y_l = |A_y|. \tag{11}$$

Since $\langle \bar{y}^2 \rangle \simeq (1/2)|y_l|^2 = (1/2)A^2$, the amplitude-expansion rate, F, is calculated from:

$$F = 2\frac{\mathrm{d}}{\mathrm{d}t}\langle \bar{y}^2 \rangle, \tag{12}$$

where $\langle \ldots \rangle$ denotes the time average over one period. Using Eqs. 8 and 12, the coefficients, γ_2 and γ_4, are obtained from:

$$\gamma_2 = 4\langle \mathrm{Re}\,y_l\ \mathrm{Re}\,\dot{y}_l \rangle A^{-2},$$
$$\gamma_4 = \gamma_{41} + \gamma_{42}, \tag{13}$$

where:

$$\gamma_{41} = -4b_2\langle \mathrm{Re}\,y_l(\mathrm{Re}\,y_l)^3 \rangle A^{-4},$$
$$\gamma_{42} = -8b_1\langle \mathrm{Re}\,y_l(\mathrm{Re}\,y_l\ \mathrm{Re}\,y_n) \rangle A^{-4}.$$

Putting Eqs. 6, 9, and 10 into Eq. 13, we get:

$$\gamma_2 = -(r - r_c),$$
$$\gamma_{41} = -\frac{3}{2}b_2,\ \gamma_{42} = -\frac{5}{3}cb_1. \tag{14}$$

For $p = p_c$ (or $r = r_c$), we can get:

$$\gamma_4 = \frac{1}{3\alpha\beta f}\left(20 - \frac{\beta}{\alpha}f\right). \tag{15}$$

Now we have determined two coefficients, γ_2 and γ_4, in Laudau's equation (Eq. 3). The properties of the two coefficients, γ_2 and γ_4, for p near p_c can easily be seen from Eqs. 14 and 15. These satisfy:

$$\gamma_2 \propto -(p_c - p) < 0, \text{ for } p < p_c,$$
$$\gamma_4 = \text{a constant independent of } p. \tag{16}$$

Figure 3 shows the plot of the amplitude-expansion rate, F, against A for $q=0.006$, $f=2.350$, and $p=58.00$ ($p_c=90.24$). The broken line shows the theoretical curve calculated from Eq. 3 using the coefficients, γ_2 and γ_4, in Eqs. 14 and 15. For the above values of q, f, and p, we get: $\gamma_2=-0.616\times10^{-2}$ and $\gamma_4=2.132$. The solid line shows the plots of the data from the computer simulations. When p is not so far from p_c, the theoretical curve is in fairly good agreement with the results of the computer simulations. The amplitude, A_u, of the unstable limit cycle can be obtained theoretically from $F=0$ thus:

$$\gamma_2 A_u^2 + \gamma_4 A_u^4 = 0. \tag{17}$$

For $A < A_u$, the amplitude-expansion rate, F, becomes negative and the trajectory shrinks towards $A=0$ (steady state), whereas for $A > A_u$ the amplitude-expansion rate becomes positive and the trajectory expands. Therefore, the trajectory with A near A_u grows apart from A_u as time goes on (unstable limit cycle). From Eq. 17, the amplitude, A_u, of the unstable limit cycle becomes:

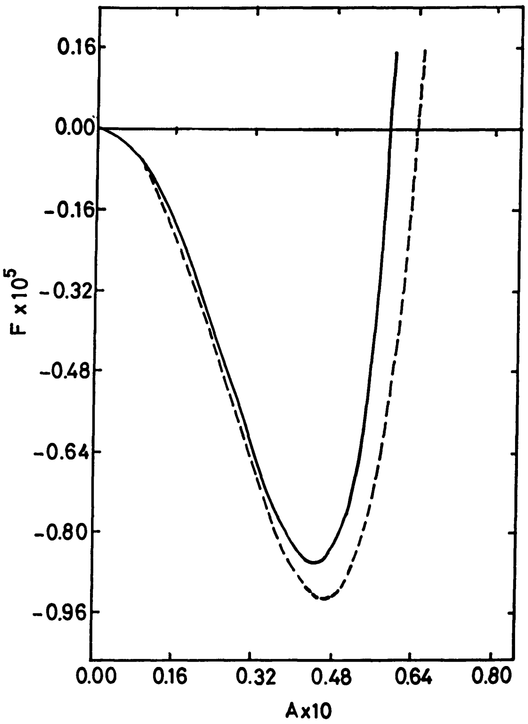

Fig. 3. Variation of amplitude expansion rate F with amplitude A of trajectory.
——: Plots of data from computer simulations, ------: theoretical curve by Landau's equation (Eq. 3) on using values of $\gamma_2=-0.616\times10^{-2}$ and $\gamma_4=2.132$ from Eqs. 14 and 15.

$$A_u = \sqrt{-\frac{\gamma_2}{\gamma_4}}. \tag{18}$$

For $p \simeq p_c$,

$$\log A_u = \frac{1}{2}\log(p_c - p) + C, \tag{19}$$

where C is a constant independent of p. In Fig. 2 the broken line represents a theoretical curve derived from Eq. 18. For $p \simeq p_c$, the gradient of the plotted line is 1/2, which agrees well with Eq. 19. For $p \ll p_c$, however, the agreement becomes less good. The reason for this discrepancy comes from the roughness of our approximations in the perturbation method.

It has been confirmed that our perturbation method (Landau theory) can explain the behavior of the unstable limit cycle near p_c fairly well. It is insufficient, however, to explain the global behavior of the limit cycles.

Global Behavior

The global behavior of the simple Oregonator model is different from the local behavior around the steady state. The estimation of the global behavior is difficult on the basis only of the theoretical analysis (linear approximation) of the local behavior. In order to examine the global behavior of the simple Oregonator model, we have made computer simulations for various values of f and p under a fixed q (=0.05). The q parameter depends on the constants determined by the elementary reactions in the FKN model.[1] These are

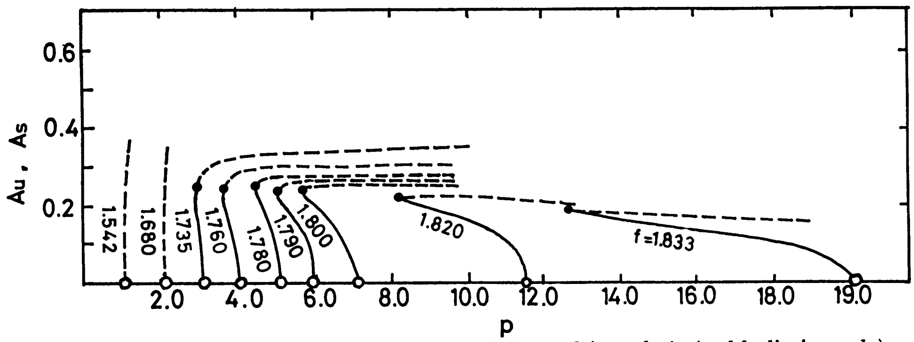

Fig. 4. Variations of amplitudes A_u (unstable limit cycle) and A_s (stable limit cycle) with parameters p and f for fixed $q=0.05$ ($f_{c_1}=0.714, f_{c_2}=1.850, f_T=1.688$).
——: Amplitude of unstable limit cycle, ------: amplitude of stable limit cycle, ○: p_c, ●: p_d.

$k_1=k_1'[H^+]^2$, $k_2=k_2'[H^+]$, $k_3=k_3'[H^+]$ and $k_4=k_4'$. The q parameter becomes:

$$q = \frac{2k_1k_4}{k_2k_3} = \frac{2k_1'k_4'}{k_2'k_3'},$$

where k_1', k_2', k_3', and k_4' are, respectively, the rate constants of the following elementary reactions in the B-Z reaction:

$$Br^- + BrO_3^- + 2H^+ \xrightarrow{k_1'} HBrO_2 + HOBr,$$

$$Br^- + HBrO_2 + H^+ \xrightarrow{k_2'} 2HOBr,$$

$$BrO_3^- + HBrO_2 + H^+ \xrightarrow{k_3'} 2BrO_2\cdot + H_2O$$

$$2HBrO_2 \xrightarrow{k_4'} HOBr + BrO_3^- + H^+.$$

As q depends only on the rate constants of the elementary reactions described above, its value can be varied by changing the temperature. Field *et al.* have determined by using known rate constants, that at 25 °C $q=8.375\times10^{-6}$. However, the dependency of every rate constant on the temperature has not been confirmed. Hence, a further examination is necessary to see whether the state of $q=0.05$ can be realized experimentally or not by changing the temperature.

We have selected such a relatively high value of q for two reasons. One is a technical reason with regard to computer simulations. In order to get the numerical value of the amplitude-expansion rate, F, continuously, we need to set q at such a high value. For a small q, for example $q=0.006$ (Fig. 1), the amplitude-expansion rate, F, becomes discontinuous near $A=A_s$. This is because the entrainment into the stable limit cycle is too strong and the trajectory does not take even one turn around the steady state. The other reason is involved with our concerns as to the qualitative property of the global behavior. As we shall see later, the global behavior of the simple Oregonator model shows a kind of phase transition as the r parameter changes.† For this purpose, the absolute value of q is not absolutely essential.

Figure 4 shows the variations in the amplitudes of the two kinds of limit cycles against p for fixed f and q values. The solid lines show the amplitudes, A_u, of the unstable limit cycles, while the broken lines show the amplitudes, A_s, of the stable limit cycles. The p_c point is the point from which a limit cycle appears. As is shown in the figure, no unstable limit cycle exists for $p>p_c$. The other transition point, p_d, is the lowest boundary value of p for the coexistence of an unstable limit cycle and a stable limit cycle. Hence, only for $p_d<p<p_c$ can two limit cycles coexist (coexistence state). Figure 5 shows the various boundary parameters on which the global behavior of the trajectory changes topologically. The f_{c_1} and f_{c_2} points are a pair of the boundary values of f inside which the steady state can be unstable; numerically, $f_{c_1}=0.714$ and $f_{c_2}=1.850$ for $q=0.05$. The T point in Fig. 5 shows the point at which three different global states coexist, where $p_d=p_c(f=f_T)$ or $r_d=r_c(f=f_T)$. We call this point, T, "a triple point"

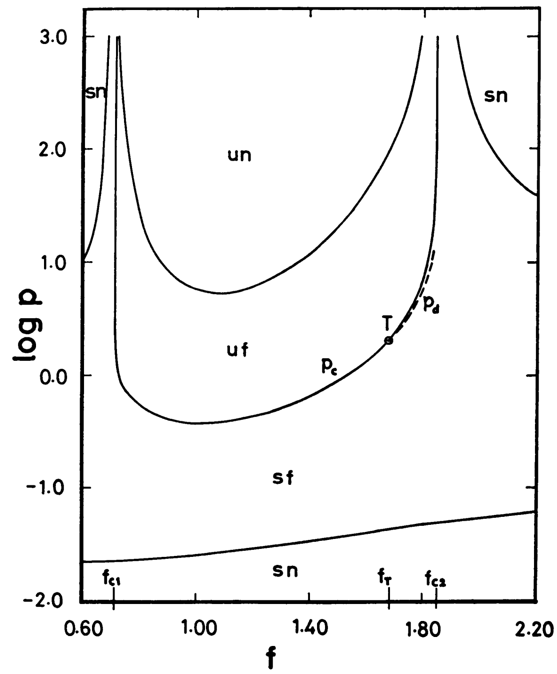

Fig. 5. Boundary parameters map for different kinds of global behavior of trajectory under $q=0.05$.
------: p_d, ⊙: triple point T, sf: stable focus, uf: unstable focus, sn: stable node, un: unstable node.

† Strictly speaking, the term phase transition is not a usual one where the system has many degrees of freedom.

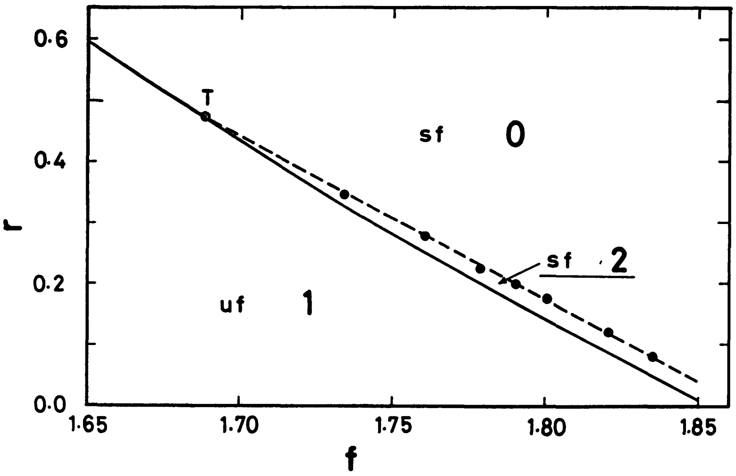

Fig. 6. Variations of $r_c \equiv 1/p_c$ and $r_d \equiv 1/p_d$ near triple point T with parameter f. (The figures in the figure represent the number of limit cycles.)
——: r_c, ●: plot point of datum from computer simulations, ⊙: triple point T, ------: line of r_d obtained by least square method, sf: stable focus, uf: unstable focus.

TABLE 1. VALUES OF BOUNDARY PARAMETERS FOR COEXISTENCE OF TWO KINDS OF LIMIT CYCLES

($q=0.05$)

f	r_c	r_d
1.8339	0.0500	0.0787
1.8200	0.0860	0.1215
1.8000	0.1399	0.1754
1.7900	0.1675	0.1994
1.7795	0.1969	0.2245
1.7603	0.2518	0.2793
1.7347	0.3275	0.3484
1.688 (f_T)	0.473 (r_T)	0.473 (r_T)

for the sake of simplicity. Figure 6 shows the variations in r_c and r_d near the triple point. The Arabic figures written in Fig. 6 represent the total number of limit cycles. The area specified by the Arabic figure 2 is the coexistence state (the coexistence of two kinds of limit cycles). The areas specified by the two figures 0 and 1 correspond to the states of a no-limit cycle and a one-limit cycle respectively. The solid line shows r_c. The black circles represent the points of r_d as obtained from computer simulations. The detailed values of r_c and r_d are shown in Table 1. The broken line has been obtained by the method of the least squares. The intersection of two lines, r_c and r_d, gives the triple point, T. The values of p_T, r_T, and f_T, which are defined by the values of p, r, and f respectively at the triple point, T, are obtained for $q=0.05$ as:

$$p_T = 2.11, \; r_T = r_c(f = f_T) = r_d(f = f_T) = 0.473,$$
$$f_T = 1.688.$$

Next we will examine the global behavior of the amplitude-expansion rate, F, under a fixed f value. The global behavior can be classified into two types: that with the coexistence state and that with no coexistence state. Our numerical simulations show that the former type can be seen for $f > f_T$, whereas the latter type can be seen for $f < f_T$. Figure 7 shows a typical example of

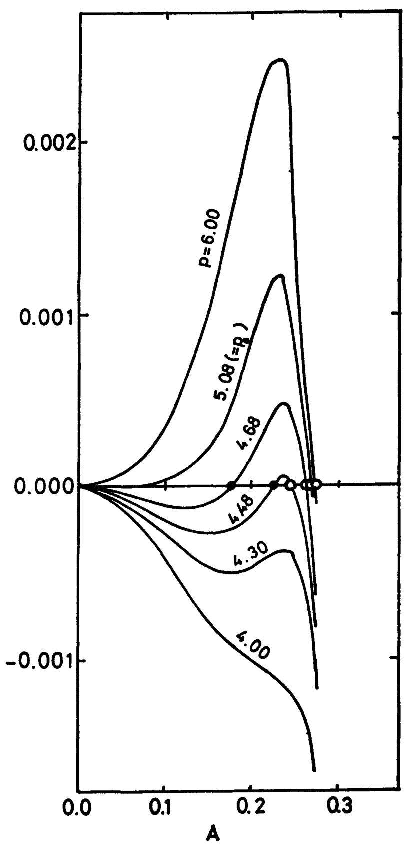

Fig. 7. Variations of amplitude expansion rate F with amplitude A of trajectory for $q=0.05$ and $f=1.7795$. ($p_c=5.080, p_d=4,454, f_{c_2}=1.850, f_T=1.688$) ●: Amplitude of unstable limit cycle, ○: amplitude of stable limit cycle.

the former type: $f=1.7795$ ($> f_T=1.688$) for $q=0.05$. Figure 8 shows one of the latter type: $f=1.100$ ($< f_T$). Here the problem arises of whether or not the coexistence

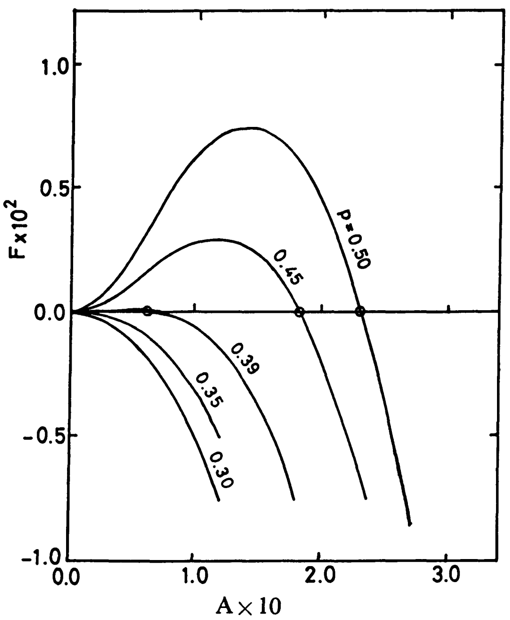

Fig. 8. Variation of amplitude expansion rate F with amplitude A of trajectory for q=0.05 and f=1.100. (p_c=0.383, f_{c_1}=0.714, f_T=1.688) ○: Amplitude of stable limit cycle.

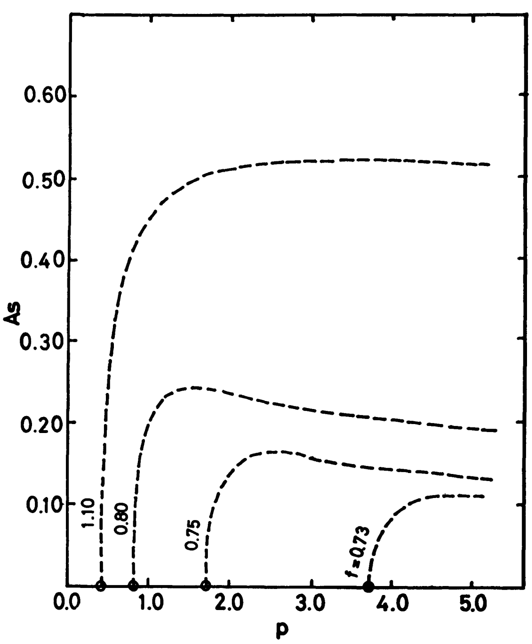

Fig. 9. Variations of amplitudes A_s (stable limit cycle) with parameters p and f for fixed q=0.05 (f<1.100, f_T=1.688, f_{c_1}=0.714).
------: Amplitude of stable limit cycle, ○: p_c.

state can exist for f near f_{c_1} in the range from f_{c_2} to f_{c_1} (the low-f side of the $f_{c_1}<f<f_{c_2}$ region). We conclude that there is no coexistence state on the low-f side of the region where case q=0.05. There are two reasons for deriving this conclusion. The first is the confirmation of the absence of an unstable limit cycle on the low-f side of the region, within the limits of accuracy of our numerical calculation by means of computer simulaions. The second is the mode of the dependence of the amplitude, A_s, on p. Figures 8 and 9 show F and A_s in a no-coexistence state. In this case, the stable limit cycle (the broken line in Fig. 9) appears immediately above p_c. This kind of behavior of the amplitudes can be seen for all cases of $f<f_T$ and is quite different from the coexistence state ($f>f_T$). In the coexistence state, the unstable limit cycle (solid line) appears from p_c, and a stable limit cycle can also exist for p below p_c, as is shown in Fig. 4.

Janz *et al.*[5] have studied the steady state stability property in an attempt to investigate a coexistence state in a simple Oregonator. By simulations for $q=8.375\times10^{-6}$, they have found two regions of the coexistence state: the low-f side and the high-f side of the region ($f_{c_1}<f<f_{c_2}$). The coexistence state investigated by us corresponds to the one on the high-f side of the region (the region of f near and below f_{c_2}). In fact, Janz *et al.* have found that the area of the coexistence state goes to zero as r exceeds a certain value††. This property is qualitatively the same as those which we have found. In our case, the boundary value of r is r_T. For $r>r_T$, the coexistence state disappears. We can not, however, find the coexistence state on the low-f side of the region for a high q ($q=5\times10^{-2}$). The most reasonable explanation for these two inconsistent results is that the coexistence state on the low-f side disappears as q exceeds a certain value. Janz *et al.* have pointed out that the area of the coexistence state on the low-f side is about 1/10 times narrower than that on the high-f side. For example, the maximum value of Δf (the width of f for which the coexistence state has been observed) is only Δf=0.038 ($\Delta f/f_{c_1}$=0.08), whereas the maximum value of Δf on the high-f side is Δf=0.38 ($\Delta f/f_{c_2}$=0.28). This means that the area of the coexistence state on the low-f side is very small, even for a small q value ($q=8\times10^{-6}$). This also suggests the disappearance of the coexistence state for a high q, and so the above explanation is reasonable.

Now we will show the qualitative change in the global behavior of the simple Oregonator model as determined by means of computer simulations. The global behavior can simply be expressed by the term "phase transition." The r_c (or p_c) and r_d (or p_d) quantities give the phase boundary, and the r_T point, the triple point. The phase corresponds to the number of limit cycles. The state with no limit cycle and one limit cycle is a single-phase state. The state with two limit cycles is the coexistence state of the two phases. This global behavior of the simple Oregonator model shows the type of statistical dynamic property. This property offers an important point of view from which to investigate the relations between the Oregonator model and other nonlinear, nonequilibrium systems.

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†† Janz *et al.* have used the k_5 parameter. The relation between k_5 and r is $r=k_5/(k_1A)$ (the notation of k_1, k_5, and A follows Janz *et al.*).

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