The Existence of an Unstable Limit Cycle in the Oregonator Model for the Belousov-Zhabotinskii Reaction

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With an Oregonator model for the mechanism of the Belousov-Zhabotinskii reaction (an oscillatory chemical system), the coexistence of a stable and an unstable limit cycle was confirmed from the results of computer simulations and the real unstable limit cycle was shown. The relation of the amplitude of the unstable limit cycles to the parameters f and p in Tyson's equation[4] was found.

The Belousov-Zhabotinskii reaction (B-Z reaction) is a well known example of an oscillatory chemical reaction. Field, Körös, and Noyes[1] presented the mechanism for this reaction in the homogeneous system and proposed a simple reaction model for sustained oscillation, which is called an Oregonator. Subsequently, Noyes *et al.*[2] Murray *et al.*[3] and Tyson[4] examined precisely the oscillation conditions based on the model. Tyson predicted the existence of a pair of stable and unstable limit cycles for a parameter p close to a critical one, p_c, in his analysis. However, he did not show any real unstable limit cycles. In this study the conditions for an unstable steady state are given over a wide range of the parameters f, p, and q in Tyson's equation; the coexistence of stable and unstable limit cycles, which is called "hard self-excitation", is confirmed for a parameter p not only close to p_c, but also far from it. The relation of the amplitudes of the unstable limit cycles to the parameters f and p is also clarified from the results of computer simulations.

The mechanism of the B-Z reaction to be expressed with the Oregonator is as follows:[2]

$$A + Y \xrightarrow{k_1} X + P, \tag{1-1}$$

$$X + Y \xrightarrow{k_2} 2P, \tag{1-2}$$

$$B + X \xrightarrow{k_3} 2X + Z, \tag{1-3}$$

$$2X \xrightarrow{k_4} B + P, \tag{1-4}$$

$$Z \xrightarrow{k_5} fY. \tag{1-5}$$

The symbols correspond to the chemical species in the B-Z reaction system as follows;

$X = HBrO_2$, $Y = Br^-$, $Z = 2Ce^{4+}$, $A = B = BrO_3^-$, $P = HOBr$.

The parameter f is a stoichiometric factor and is twice the number of Br^- ions generated per Ce^{4+} to be reduced. During the following calculations, it is assumed that the concentrations of A and B remain constant, effectively treating the system as open.

The kinetic behavior of the reaction (1) was represented by Tyson[4] with the following dimensionless equations:

$$\varepsilon\frac{dx}{d\tau} = x + y - qx^2 - xy, \tag{2-1}$$

$$\frac{dy}{d\tau} = -y + fz - xy, \tag{2-2}$$

$$p\frac{dz}{d\tau} = x - z, \tag{2-3}$$

Here x, y, and z *etc.* are the variables including X, Y, Z, A, B, and k_i, *etc.* which represent the concentrations of species and the rate constants, *etc.* as follows:

$$\begin{aligned} x &= k_2(k_1A)^{-1}X, \\ y &= k_2(k_3B)^{-1}Y, \\ z &= k_2k_5(k_1k_3AB)^{-1}Z, \\ p &= k_1k_5^{-1}A, \\ q &= 2k_1k_4(k_2k_3B)^{-1}A, \\ \varepsilon &= k_1A(k_3B)^{-1}, \\ \tau &= k_1At. \end{aligned}$$

The constant solution ("steady state") of Eq. 2 without the origin ($x=y=z=0$) is

$$\left.\begin{aligned} x_0 = z_0 &= \{1-f-q+\sqrt{(1-f-q)^2+4q(f+1)}\}(2q)^{-1} \\ y_0 &= fx_0(1+x_0)^{-1} \end{aligned}\right\}. \tag{3}$$

In order to examine the trajectory in the neighborhood of the steady state, Eq. 2 is expressed in terms of deviations from the steady state, which are $\bar{x}=x-x_0$, $\bar{y}=y-y_0$, $\bar{z}=z-z_0$, as follows:

$$\varepsilon\frac{d\bar{x}}{d\tau} = -\alpha\bar{x} - \beta\bar{y} - q\bar{x}^2 - \bar{x}\bar{y}, \tag{4-1}$$

$$\frac{d\bar{y}}{d\tau} = -\gamma\bar{x} - \delta\bar{y} + f\bar{z} - \bar{x}\bar{y}, \tag{4-2}$$

$$p\frac{d\bar{z}}{d\tau} = \bar{x} - \bar{z}, \tag{4-3}$$

where

$$\left.\begin{aligned} \alpha &= -1 + y_0 + 2qx_0 = qx_0 + y_0x_0^{-1} > 0 \\ \beta &= x_0 - 1 > 0, \qquad \text{for } q<1 \\ \gamma &= y_0 > 0 \\ \delta &= x_0 + 1 > 0. \end{aligned}\right\}. \tag{4-4}$$

When $\varepsilon \to 0$ as in the real B-Z reaction,[1] the following condition is maintained, from Eq. 4-1:

$$q\bar{x}^2 + (\alpha+\bar{y})\bar{x} + \beta\bar{y} = 0.$$

Thus

$$X(\bar{y}) = \bar{x} = \{-(\alpha+\bar{y}) \pm \sqrt{(\alpha+\bar{y})^2 - 4q\beta\bar{y}}\}(2q)^{-1}. \tag{5}$$

Here, only the positive sign of $\pm$ in Eq. 5 is taken, because, if the negative sign is taken, $x<0$, this would a negative concentration, which is physically unacceptable.

From Eqs. 5, 4-2, and 4-3, the following two ordinary differential equations can be obtained:

$$\left.\begin{aligned}\frac{d\bar{y}}{d\tau} &= -\delta\bar{y} + f\bar{z} - (\gamma+\bar{y})X(\bar{y}) = Y(\bar{y},\bar{z})\\ \frac{d\bar{z}}{d\tau} &= \frac{1}{p}X(\bar{y}) - \frac{1}{p}\bar{z} = Z(\bar{y},\bar{z})\end{aligned}\right\}. \tag{6}$$

Since $\bar{y}\ll y_0$, $\bar{z}\ll z_0$, Eq. 6 can be linearized as follows:

$$\left.\begin{aligned}\frac{d\bar{y}}{d\tau} &= Y_{\bar{y}}\bar{y} + Y_{\bar{z}}\bar{z}\\ \frac{d\bar{z}}{d\tau} &= Z_{\bar{y}}\bar{y} + Z_{\bar{z}}\bar{z},\end{aligned}\right\}, \tag{7}$$

where

$$Y_{\bar{y}} = \left(\frac{\partial Y(\bar{y},\bar{z})}{\partial\bar{y}}\right)_{\left\{\substack{\bar{y}=0\\ \bar{z}=0}\right.} = \frac{\beta\gamma-\alpha\delta}{\alpha}, \tag{8-1}$$

$$Y_{\bar{z}} = \left(\frac{\partial Y(\bar{y},\bar{z})}{\partial\bar{z}}\right)_{\left\{\substack{\bar{y}=0\\ \bar{z}=0}\right.} = f, \tag{8-2}$$

$$Z_{\bar{y}} = \left(\frac{\partial Z(\bar{y},\bar{z})}{\partial\bar{y}}\right)_{\left\{\substack{\bar{y}=0\\ \bar{z}=0}\right.} = -\frac{\beta}{p\alpha}, \tag{8-3}$$

$$Z_{\bar{z}} = \left(\frac{\partial Z(\bar{y},\bar{z})}{\partial\bar{z}}\right)_{\left\{\substack{\bar{y}=0\\ \bar{z}=0}\right.} = -\frac{1}{p}. \tag{8-4}$$

The behaviors of $\bar{y}$ and $\bar{z}$ in the neighborhood of the steady state are determined by the eigenvalues, λ, of the matrix

$$A = \begin{pmatrix} Y_{\bar{y}} & Y_{\bar{z}}\\ Z_{\bar{y}} & Z_{\bar{z}}\end{pmatrix}$$

which satisfies the following secular equation

$$\lambda^2 - Tr\lambda + \mathrm{Det} = 0,$$

where

$$Tr = Y_{\bar{y}} + Z_{\bar{z}} = \frac{\beta\gamma-\alpha\delta}{\alpha} - \frac{1}{p},$$

$$\mathrm{Det} = Y_{\bar{y}}Z_{\bar{z}} - Y_{\bar{z}}Z_{\bar{y}} = \frac{\alpha\delta-\beta\gamma+f\beta}{p\alpha}.$$

Stability of Steady State

The boundary condition that determines the stability of a steady state for the periodic solutions is given by $Tr=0$, that is

$$Tr = \frac{\beta\gamma-\alpha\delta}{\alpha} - \frac{1}{p} = 0. \tag{9-1}$$

As is obvious from Eqs. 3 and 4-4, each of α, β, γ, and δ can be a function of q and f. Equation 9-1, then, can be generally represented as follows:

$$\mathrm{F}(f,p,q) = 0. \tag{9-2}$$

Here, $\mathrm{F}(f, p, q)=(\beta\gamma-\alpha\delta)/\alpha-1/p$. Thus, for a certain fixed set of two values from three parameters the remaining parameter which satisfies Eq. 9-2 gives a critical value. For p fixed, Eq. 9 gives a critical value of f as a function of q, which is shown in Fig. 1. For a value of q less than 0.0809, the critical f takes two values, f_{c_1} and f_{c_2}, where $f_{c_1}<f_{c_2}$. If $f_{c_1}<f<f_{c_2}$, $Tr>0$ and the steady state is unstable. On the other hand, if $f<f_{c_1}$ or $f>f_{c_2}$, $\mathrm{Tr}<0$ and the steady state is stable. For example, when $p=\infty$ and $q=0$, $f_{c_1}=0.5$, and $f_{c_2}=1+\sqrt{2}=2.414$. The region of f in which a steady state is unstable becomes narrower with increasing values of q, as shown in Fig. 1.

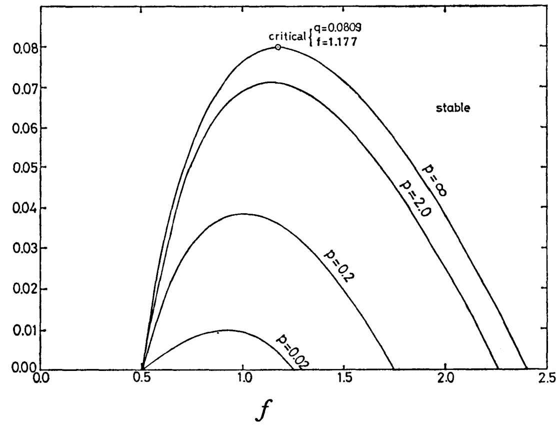

Fig. 1. Stability of the steady state as a function of parameters q and f for the various values of p. The steady state is unstable for the values of f and q inside a curve for p fixed.

For q fixed, a critical p, p_c, is given as a function of f by Eq. 9 as follows:

$$p_c = \frac{\alpha}{\beta\gamma-\alpha\delta} \tag{10}$$

If $p<p_c$, $Tr<0$ and then the steady state is stable; if $p>p_c$, $Tr>0$ and then the steady state is unstable.

The boundary condition for whether a trajectory around a steady state is a periodic spiral or not, that is, whether a steady state is a focus or node, is given by $Tr^2=4\mathrm{Det}$. The critical parameter p, $p_\pm$, is represented by

$$p_\pm = \{(p_c^{-1}+2\xi) \pm 2\sqrt{\xi p_c^{-1}+\xi^2}\}p_c^2, \tag{11}$$

where

$$\xi = \mathrm{Det}\cdot p = \frac{\alpha\delta-\beta\gamma+f\beta}{\alpha}.$$

Since $p_\pm$ is a function of q and f only, its value can be determined for a certain set of q and f values. If $p_-<p<p_+$, $Tr^2<4\mathrm{Det}$ and a steady state is a focus; on the other hand, if $p<p_-$ or $p>p_+$, $Tr^2>4\mathrm{Det}$ and it is a node.

Tyson[4] calculated p_c and $p_\pm$ by using an approximation which is calculated for a very low value of q. Here, without the approximation, p_c and $p_\pm$ were calculated directly from Eqs. 3, 4-4, 10, and 11 for q fixed. A result for $q=0.006$ is shown in Fig. 2, which represents a f-p parameter phase space. It differs from the approximate result obtained by Tyson in the regions near the values of 0.5 and 1.0 of f.

If f and p have the values in the unstable focus region (uf) in Fig. 2, a steady state is unstable, the behavior of the trajectory surrounding it is periodic, and the existence of a stable limit cycle can be predicted: that is the situation called "soft self-excitation". The real limit cycle was obtained by Tyson[4] with a numerical integration of Eq. 2 for $dx/d\tau=0$ or $\varepsilon=0$.

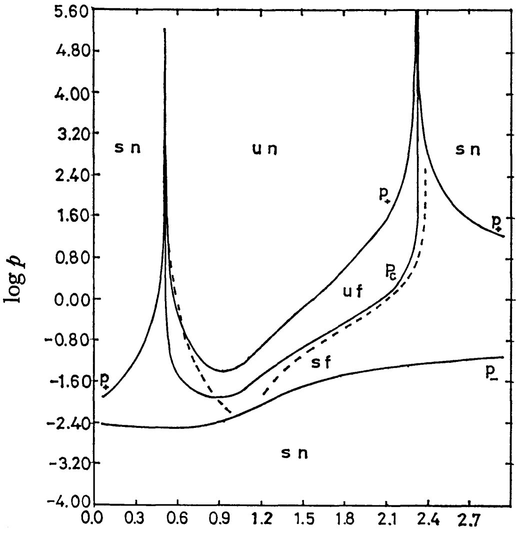

Fig. 2. Stability of the steady state and periodicity of the trajectory as a function of the parameter p and f for $q=0.006$.
------: Tyson's approximate expression of p_c for $q=0.006$, sn: stable node, sf: stable focus, un: unstable node, uf: unstable focus.

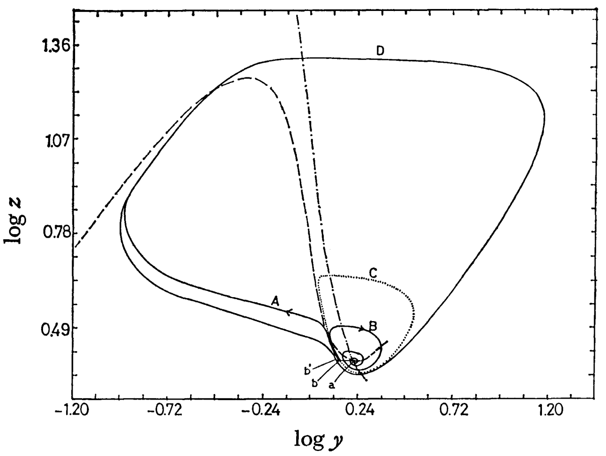

Fig. 3. Phase plane plot of $\log z$ *vs.* $\log y$ obtained numerical integration of Eq. 2 under $\varepsilon\to 0$ for $q=0.006$, $f=2.350$, and $p=2.0$.
A: Trajectory to reach a stable limit cycle (initial values; $y=1.411$, $z=2.444$), B: trajectory to reach a steady state (initial values; $y=1.412$, $z=2.444$), C: unstable limit cycle, D: stable limit cycle, a: steady state, ab: *AMP*, ----: solution of Eq. 2 for $\mathrm{d}x/\mathrm{d}\tau=0$ and $\mathrm{d}y/\mathrm{d}\tau=0$, —·—·: solution of Eq. 2 for $\mathrm{d}x/\mathrm{d}\tau=0$ and $\mathrm{d}z/\mathrm{d}\tau=0$.

Coexistence of Stable and Unstable Limit Cycles[5)]

There should be no stable limit cycle in the case where f and p have the values in the stable focus (sf) region in Fig. 2, unless an unstable limit cycle surrounds a stable focus (Poincarè-Bendixon's theorem). In regard to the Oregonator, it was confirmed with computer simulations that a stable limit cycle coexists with an unstable limit cycle which surrounds a stable focus in the case of $p_c>p>p_d$, where p_d is a critical parameter for the existence of an unstable limit cycle. That is, the situation called "hard self-excitation" can appear not only for the condition of $p\simeq p_c$, but also for every p value in the range of $p_c>p>p_d$, even when $p_c\gg p_d$. For an example, in the case of $q=0.006$ and $p=\infty$, $f_{c_1}=0.519$, and $f_{c_2}=2.354$ (Fig. 1), $p_+=1.584\times 10^5$, $p_-=5.141\times 10^{-2}$, $p_c=90.24$ (Fig. 2), and $p_d=0.849$ (Fig. 5). These values come from the results of numerical calculated solutions of Eq. 2 under $\varepsilon\to 0$ for various values of p. The hard self-excitation under this condition is shown in Fig. 3. In the situation, there could be two kinds of trajectories, A and B in Fig. 3, starting from the two different initial values near to each other, one of which asymptotically reaches a stable steady state, and the other a stable limit cycle. In the former case the oscillation is damped, while in the latter it is sustained. These two kinds of temporal changes on the variable y are shown in Fig. 4. In this case, the bifurcation can occur with a small change of a value of p for a certain initial value. In this situation, a final behavior of a system is decided due to the result of a fluctuation in the initial values of y and z, or in a parameter p. However, the hard self-excitation phenomenaon has not yet been found experimentally in

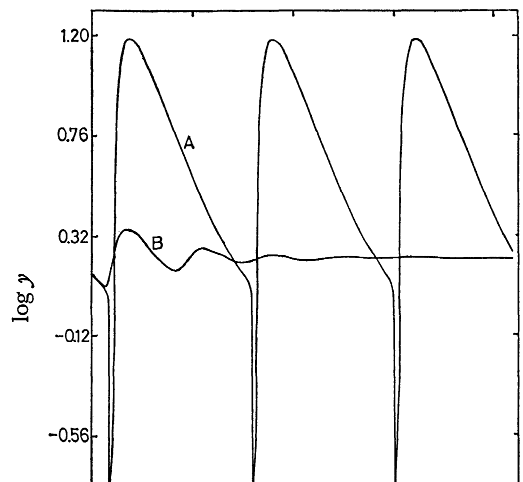

Fig. 4. Temporal behaviors of log y for $q=0.006$, $f=2.350$ and $p=2.0$.
A: Sustained oscillation (initial values; $y=1.411$, $z=2.444$), B: damped oscillation (initial values; $y=1.412$, $z=2.444$).

a real B-Z reaction. The chemical equation, Eq. 1-5 in the Oregonator corresponds to the real reaction:

$$2Ce^{4+}+\frac{1}{2}BrCH(COOH)_2+H_2O\longrightarrow$$
$$2Ce^{3+}+\frac{1}{2}HCOOH+CO_2+\frac{1}{2}Br^-+\frac{5}{2}H^+.$$

Therefore, the value of k_5 includes not only the rate constant of this reaction, but also the concentration of $BrCH(COOH)_2$, (BrMA). Since $p=k_1k_5^{-1}$ A, an

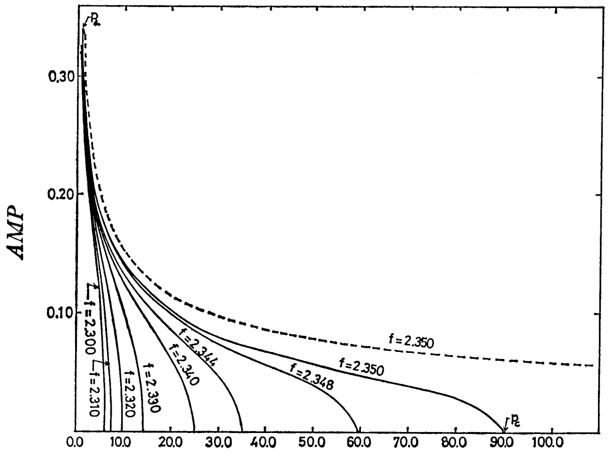

Fig. 5. Plot of AMP *vs.* p for $q=0.006$.
——: Amplitude of unstable limit cycle, $\overline{ab}$ in Fig. 3, ----: amplitude of stable limit cycle, $\overline{ab}'$ in Fig. 3.

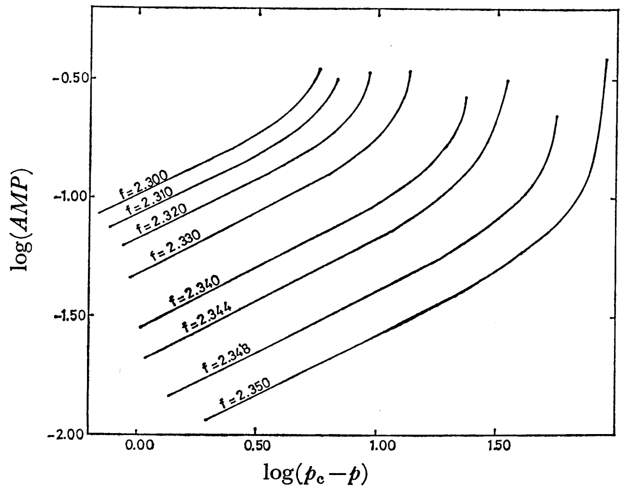

Fig. 6. Plot of $\log(AMP)$ *vs.* $\log(p_c-p)$.

increase of temperature, which increases the value of the rate constant, or of the concentration of BrMA should result in a decrease of p. If p could reach a value in the range of $p_d<p<p_c$ through as adjustment of these conditions, it may be possible to realize a hard self-excitation in the real B-Z reaction.

Relation of Amplitudes of Unstable Limit Cycles with p

In Fig. 3, a steady state ($y=y_0$, $z=z_0$) is represented by the symbol "a", and the point which a line $z=z_0$ intersects an unstable limit cycle is denoted by the symbol "b"; then it is convenient to define the distance, $\overline{ab}$, between the points "a" and "b" as the amplitude of an unstable limit cycle, AMP. These amplitudes for various values of f and p were obtained from computer simulations. Figure 5 shows the plots of AMP against p for various f values and Fig. 6 shows the plots of $\log(AMP)$ against $\log(p_c-p)$. These are linear with a slope of 1/2 in the range of low values of (p_c-p), but $\log(AMP)$ increases rapidly with $\log(p_c-p)$ in its high value range. This relation and the behavior of periodic trajectories in the hard self-excitation can be treated quantitatively with Landau's theory, in which a transition from a steady flow to a turbulent one in a stream could be elucidated. The quantitative treatment of this problem will be dealt with later.

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