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On Behaviors of a New Chemical Reaction Model Showing Hard Oscillations

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The behavior of a new chemical reaction model was studied and the existence of hard oscillations was confirmed. This chemical reaction model is useful because it is easy to apply to investigations of the behavior of a chemically oscillating system surrounded by membranes or in a well-stirred continuous flow reactor. The latter was discussed relating to the chaotic oscillations due to the Belousov-Zhabotinskii reaction in a well-stirred continuous flow reactor reported by Schmitz *et al.*

Until now many papers about behaviors of chemical systems far from equilibrium states have been presented.$^{1-20)}$ A system far from an equilibrium state occasionally shows a characteristic phenomenon like chemical oscillations.$^{1-6)}$ The representative exemplified phenomenon is observed on the Belousov-Zhabotinskii reaction.$^{1)}$ This chemical system has been investigated by many investigators and especially Noyes *et al.* of Oregon University studied in detail$^{11)}$ and proposed a well-known chemical reaction model called "Oregonator."$^{4)}$ The fundamental theory of nonequilibrium thermodynamics has been developed mainly by Prigogine and his school.$^{2)}$ According to them, the steady state of the system far from an equilibrium state is not always stable and transits to formation of a new type of structures when the system changes beyond a critical point of instability. These structures, which are occasionally heterogeneous and oscillatory states, are called the dissipative structures. It is quite remarkable that some of the most spectacular aspect of biological activities, such as control of cellular division, cellular differentiation and morphogenesis, can be modeled in terms of dissipative structures.$^{2,12)}$

We have studied a model chemical system having multiple steady states in order to investigate the chemically oscillatory phenomena,$^{13)}$ and these studies were applied to the problem of absolutely asymmetric synthesis.$^{14)}$ In this paper, a new chemical reaction model, which is derived from our model of chemical oscillations,$^{13)}$ is proposed and studied in detail. This chemical system shows stable oscillations around a stable steady state and pulse generations around the sustained oscillatory state with a small amplitude.

The present chemical reaction model can be applied to investigate the behavior of a chemical oscillatory system which is enclosed by a membrane or in a well-stirred continuous flow reactor. It seems that the application to the latter system is useful for interpreting the chaotic oscillations of the Belousov-Zhabotinskii reaction in a well-stirred continuous flow reactor observed by Schmitz *et al.*$^{15)}$

Behaviors of Chemical Reaction Model

Chemical Reaction Model. We consider the following reaction system;

$$P \xrightarrow{k_1} E, \tag{R-1}$$

$$E + X \xrightarrow{k_2} X + R, \tag{R-2}$$

$$A + 2X + E \underset{k_4}{\overset{k_3}{\rightleftharpoons}} 3X + E, \tag{R-3}$$

$$B + X \underset{k_6}{\overset{k_5}{\rightleftharpoons}} C, \tag{R-4}$$

$$E \xrightarrow{k_7} S, \tag{R-5}$$

$$X \xrightarrow{k_8} T. \tag{R-6}$$

These reaction steps proceed homogeneously at constant temperature and pressure. The concentrations of P, A, B, and C are kept constant by means of an external control in order to sustain the system far from equilibrium. E and X are the reaction intermediates and the rates of changes in the concentrations of E and X are expressed respectively by

$$\frac{dE}{dt} = k_1P - k_2EX - k_7E, \tag{1}$$

$$\frac{dX}{dt} = k_3AEX^2 - k_4EX^3 - k_5BX + k_6C - k_8X. \tag{2}$$

In order to study the behavior of this chemical system at the steady state, the conditions $dE/dt=0$ and $dX/dt=0$ are applied to Eqs. 1 and 2 to obtain

$$k_1P - k_2EX - k_7E = 0, \tag{3}$$

$$k_3AEX^2 - k_4EX^3 - k_5BX + k_6C - k_8X = 0. \tag{4}$$

We put $k_7=k_8=\alpha$ hereafter for simplicity. The steady state values of X and E were obtained by solving these equations and plotted in Fig. 1 as a function of α for various values of P. The solid and dotted portions indicate stable and unstable steady states, respectively. Parameter values used are as follows;

$A=1.332$, $B=5.02$, $C=5.35$, $k_1=0.1$, $k_2=0.476$,
$k_3=100.0$, $k_4=48.64$, $k_5=10.0$, $k_6=1.0$,
$P=1.50$(a), 2.0(b), 2.5(c), 2.9(d), and 3.2(e).

These parameter values were also used for study of a chemical oscillation model in the preceding paper.$^{13)}$ In the case (e), the steady state is stable in a range of adequately small α values and changes into unstable when α increases beyond a critical point near $\alpha=0.014$ and again returns stable in a range beyond a critical point near $\alpha=0.224$; that is, it is expected that a sustained oscillatory state is realized in the dotted line region. To confirm this expectation, Eqs. 1 and 2 were solved for $P=3.2$ by the Runge-Kutta method with a digital computer. Three of calculated results are shown in Fig. 2. In the case (a), the amplitude of oscillations is small, but in the cases (b) and (c), the amplitudes are equally large. In Fig.

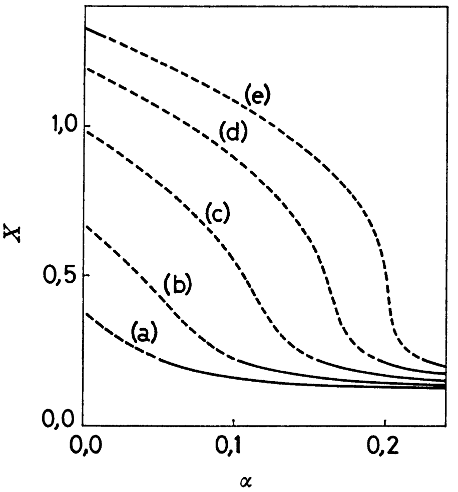

Fig. 1. Plots of steady state concentration of X obtained from Eqs. 3 and 4 against α. Solid lines represent stable steady states and dotted lines represent unstable ones. Parameter values used are; $A=1.332$, $B=5.02$, $C=5.35$, $k_1=0.1$, $k_2=0.476$, $k_3=100.0$, $k_4=48.64$, $k_5=10.0$, $k_6=1.0$, (a) $P=1.50$, (b) $P=2.0$, (c) $P=2.5$, (d) $P=2.9$, and (e) $P=3.2$.

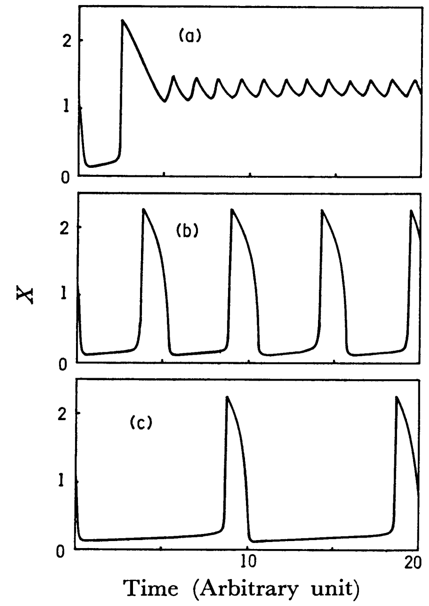

Fig. 2. Results of numerical solution of Eqs. 1 and 2 for $P=3.2$, (a) $\alpha=0.015$, (b) $\alpha=0.14$, and (c) $\alpha=0.222$. Other paremeter values used are the same with those of Fig. 1. The steady states are unstable for these parameter values and oscillations occur.

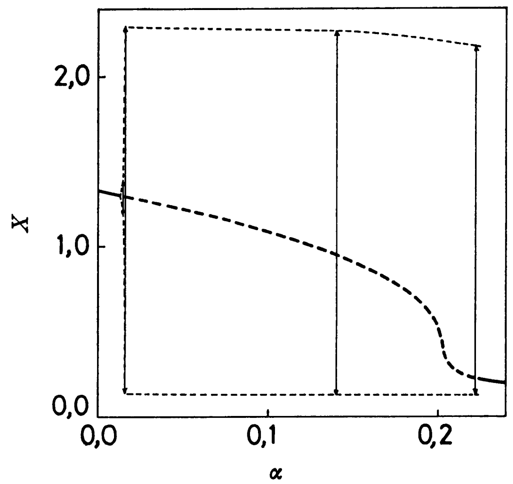

Fig. 3. Plot of amplitude of oscillations against α value determined from Eqs. 1 and 2. All the parameter values are the same with those of Fig. 1. Two types of transition points are shown. At the transition point near $\alpha=0.014$, the amplitude increases continuously with an increasing value of α, while a hard oscillation occurs at the transition point near about $\alpha=0.2238$. See Fig. 5.

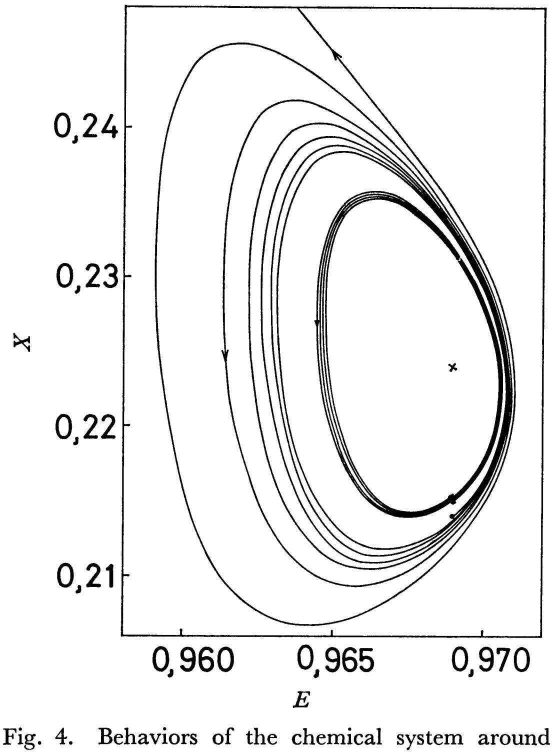

Fig. 4. Behaviors of the chemical system around the stable steady state. × indicates the stable steady state. When a calculation is started from the initial state of $X=0.215$ and $E=0.969$, the chemical system falls into the stable steady state and it is started from the initial state of $X=0.214$ and $E=0.969$, the system falls into the stable oscillatory state. $\alpha=0.2237$. × ($X=0.224$, $E=0.9689$).

3, the amplitude of oscillation is plotted against α. The upper and lower thin dotted lines show the width of oscillations. The thick solid and dotted line indicates stable and unstable steady state, respectively. The amplitude of oscillation decreases drastically at the critical point of $\alpha=0.2238$, and this suggests coexistence of stable oscillatory and stable non-oscillatory states, where the oscillatory states are not self-induced but are initiated by a finite perturbation at the stable non-oscillatory states. This phenomenon is called hard oscillations.[16] Actually, it was confirmed from calculations of Eqs. 1 and 2 at $\alpha=0.2237$ that a sustained oscillatory state encloses a stable steady state. The enlarged picture of a region around the stable steady state is shown in Fig. 4. When a calculation is started

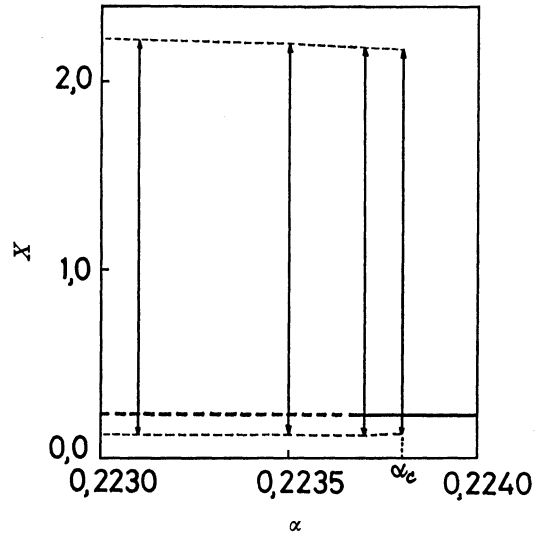

Fig. 5. Amplitude behavior of oscillations at the transition point. $\alpha_C=0.2238$.

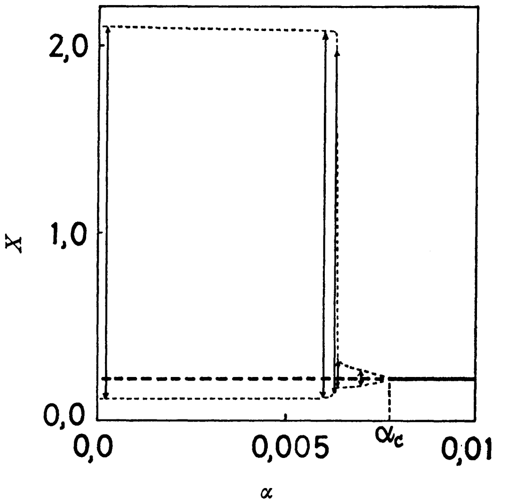

Fig. 6. Amplitude behavior of oscillations near $\alpha=0.0077$ for $k_1=0.5$, $k_2=2.38$, and $P=1.05$. Other parameter values are the same with those of Fig. 1. $\alpha_C=0.0077$.

from the initial state of $X=0.215$ and $E=0.969$, the chemical system falls into the stable steady state and when it is started from the initial state of $X=0.214$ and $E=0.969$, the system falls into the stable oscillatory state. In this case, both the oscillatory and non-oscillatory states coexist, and the transition from (or to) sustained oscillatory state to (or from) non-oscillatory state has a threshold.[16]

The diagram relating the amplitude of hard oscillations to α is depicted in Fig. 5. Hysteresis behavior would be observed for the transition between the sustained oscillatory state and the stable steady state. When α decreases from 0.224 to lower values, the steady non-oscillatory state would result until α becomes to 0.22366; at this point the transition from the non-oscillatory to the oscillatory states would occur. When α is lower than 0.22366, only the oscillatory state appears. Reversely, the oscillations would persist until α increases beyond 0.2238. This situation results in a hysteresis phenomenon.

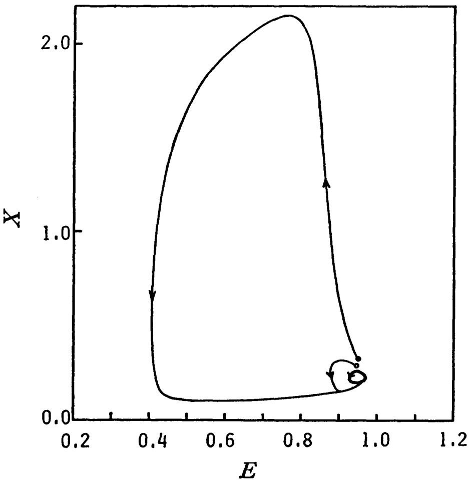

Fig. 7. Behaviors of the chemical system starting from two different initial states. When it starts from ($X=0.33$, $E=0.95$), the chemical system goes on a long excursion before falling into the stable oscillatory state displayed with a thick closed line. While, when it start from ($X=0.30$, $E=0.95$), it falls into the stable oscillatory state accompanying damped oscillations. $\alpha=0.0072$.

Excitation Around a Sustained Oscillatory State. The solution of Eqs. 1 and 2 are shown in Fig. 6 for $k_1=0.5$, $k_2=2.38$, and $P=1.05$. The amplitude of oscillation changes drastically at about $\alpha=0.0064$, and the amplitude decreases gradually with increasing α and eventually disappears when the stability of steady state becomes stable. When $\alpha=0.0072$, this chemical system has an oscillatory state with a small amplitude. This oscillatory state is shown with a closed cycle drawn by thick line in Fig. 7. The chemical system falls into this stable oscillatory state from any initial states, although the routes to the oscillatory state depend greatly on the initial states. When it starts from the state ($X=0.33$, $E=0.95$), the chemical system goes on a long excursion before falling into the sustained oscillatory state, and when it starts from the state ($X=0.30$, $E=0.95$), it falls into the stable oscillatory state accompanying a damped oscillatory behavior. Only pulse generation is observed when the system is brought by a certain distance from the oscillatory state. This system shows therefore the phenomenon of pulse generation with a threshold.[5,13,17,18]

Application to a Membrane-chemical System

Now let us consider a membrane-chemical system which consists of the chemically oscillatory model (R-1)—(R-4) surrounded by a membrane. This model was used in our preceding paper[13] to investigate the chemically oscillatory behaviors. In this system, the concentrations of A, B, C, and P inside the membrane are kept constant by means of an external control, and the concentrations of E and X outside the membrane are maintained to be zero. All of the chemical species are homogeneously distributed inside the membrane. Then, the rates of permeation of E and X through the membrane are expressed as;

$$J_E = h_E E, \tag{5}$$

$$J_X = h_X X, \tag{6}$$

where h_E and h_X are the permeation coefficients of E and X, respectively. Then, the rate equations of E and X inside the membrane are written as;

$$\frac{dE}{dt} = k_1 P - k_2 EX - h_E ES/V, \tag{7}$$

$$\frac{dX}{dt} = k_3 AEX^2 - k_4 EX^3 - k_5 BX + k_6 C - h_X XS/V, \tag{8}$$

where S and V are the surface area and the volume of the reaction region surrounded by the membrane, respectively. If we put $h_E S/V = h_X S/V = \alpha$, Eqs. 7 and 8 become the same type equations with Eqs. 1 and 2, respectively. Therefore, we can discuss the behaviors of the chemical system surrounded by a membrane with the completely same method described in the preceding section.

Every living system is constructed of cells and every cell is surrounded by a lipid bilayer membrane which transports substances necessary for living process, and, therefore, it is important to explain behaviors of the chemically oscillatory system surrounded by membrane.[3,6,10)]

Behaviors of the Chemically Oscillatory Model in a Well-stirred Continuous Flow Reactor

In this section, let us study behaviors of the chemically oscillatory model (R-1)—(R-4) in a well-stirred continuous flow reactor. Schmitz *et al.* studied the behaviors of the Belousov-Zhabotinskii reaction in a well-stirred continuous flow reactor and observed chaotic oscillations in a certain region of flow rate.15) They explained this behavior based on the idea of Rösseler;19) that is, a phase point moves on a folded surface with an unstable steady state in a phase space of three variables, and hysteresis transition across a fold generates chaotic behaviors.

Noyes *et al.*20) reported that chaotic oscillations of the Oregonator can be explained by some modifications of their chemical model. They used a model containing seven intermediates and analyzed the stability of steady states by introducing a new variable P, which represents the concentration of the intermediate HOBr. There exists a certain value of P where the stability of steady state reverses, and the linkage of P with other chemical species results in random oscillations of large and small amplitudes under suitable conditions.

The present investigation shows that the chaotic behaviors can be explained without any modification of the reaction steps of the original model and, therefore, the chaotic oscillations of the Oregonator observed by Schmitz *et al.*15) can be also explained by the present method, which is quite different from the method by Noyes *et al.*20)

Now let us consider a well-stirred continuous flow reactor, in which a series of reactions (R-1)—(R-4) is taking place with a constant feed of a fresh raw solution and a continuous removal of a reacted solution. The feed solution is composed of chemical species A, B, C, and P and the reacted solution is composed of A, B, C, E, P, R, and X. The total flow rate of the solution into the reactor is J and the volume of the flow reactor is V. We put J/V as β for abbreviation.

The material balance of these chemical species in the reactor is expressed as

$$\frac{dP}{dt} = \beta(P_o - P) - k_1'P, \tag{9}$$

$$\frac{dA}{dt} = \beta(A_o - A) - k_3'AEX^2 + k_4'EX^3, \tag{10}$$

$$\frac{dB}{dt} = \beta(B_o - B) - k_5'BX + k_6'C, \tag{11}$$

$$\frac{dC}{dt} = \beta(C_o - C) + k_5'BX - k_6'C, \tag{12}$$

$$\frac{dE}{dt} = k_1'P - k_2'EX - \beta E, \tag{13}$$

$$\frac{dX}{dt} = k_3'AEX^2 - k_4'EX^3 - k_5'BX + k_6'C - \beta X. \tag{14}$$

Here A_o, B_o, C_o, and P_o are concentrations in the feed solution and A, B, C, and P are uniform concentrations in the reactor. The terms including β represent flow terms.

Equation 9 is solved to give the solution

$$P = \frac{\beta P_o}{\beta + k_1'} + \left(P' - \frac{\beta P_o}{\beta + k_1'}\right) e^{-(\beta + k_1')t}, \tag{15}$$

where P' is an initial value of P. When t is adequately large, P becomes to $\beta P_o/(\beta + k_1')$, independently of P' value. Here we adopt the following values; $k_1' = 0.5 \times 10^{-5}$, $k_2' = 2.38$, $k_3' = 1.0 \times 10^{-3}$, $k_4' = 48.64$, $k_5' = 1.0 \times 10^{-4}$, and $k_6' = 1.0 \times 10^{-5}$. Then, P is nearly equal to P_o when β is sufficiently larger than k_1'. The values of A, B, and C are similarly discussed and it was shown that their final concentrations are nearly equal to A_o, B_o, and C_o, respectively.21) When we put $P_o = 1.05 \times 10^5$, $A_o = 1.332 \times 10^5$, $B_o = 5.02 \times 10^5$, and $C_o = 5.35 \times 10^5$, the values of $k_1'P_o$, $k_3'A_o$, $k_5'B_o$, and $k_6'C_o$ are equal to those of $k_1 P$, $k_3 A$, $k_5 B$, and $k_6 C$, which were used in the preceding sections. Then, we can discuss the behaviors of the chemical system (R-1)—(R-4) in a well-stirred continuous flow reactor by the aid of the results shown in Figs. 6 and 7, where α is exactly equivalent to β. In this situation there is an abrupt change in amplitude at about $\beta = 0.0064$ and a small deviation causes pulse generation around the sustained oscillatory state, as shown already. Therefore, small random deviations of flow rate cause randomly large or small amplitude oscillations. Moreover, any actual system is under influences of fluctuation. Then, we have to use the rate equations including fluctuation terms in order to investigate the behaviors of the chemical system at a critical point.13)

$$\frac{dE}{dt} = k_1'P_o - k_2'EX - [\beta + \beta' F(t)]E + \gamma G(t), \tag{16}$$

$$\frac{\mathrm{d}X}{\mathrm{d}t} = k_3'A_0EX^2 - k_4'EX^3 - k_5'B_0X + k_6'C_0 - [\beta+\beta'F(t)]X + \delta H(t), \qquad (17)$$

where $F(t)$, $G(t)$, and $H(t)$ are the fluctuation terms of Gaussian type.[13] The average values $\langle F(t)\rangle$, $\langle G(t)\rangle$, and $\langle H(t)\rangle$ are zero and the standard deviations are set to be 0.1. The coefficients β', γ, and δ represent the strengths of fluctuations, and $\beta'F(t)$ corresponds to the fluctuation of flow rate and $\gamma G(t)$ and $\delta H(t)$ correspond to the concentration fluctuations of E and X, respectively. Figure 8 illustrates behaviors of the chemical reaction model in a well-stirred continuous flow reactor for various values of β. At lower values of flow rate J, only large amplitude oscillations appear and in some range of flow rate, shown by (c) and (d), both large and small amplitude oscillations appear randomly. When the flow rate increases much more, only small amplitude oscillations occur and fade out, as shown by the cases of (e) and (f). These results agree essentially well with that of Schmitz *et al.*[15]

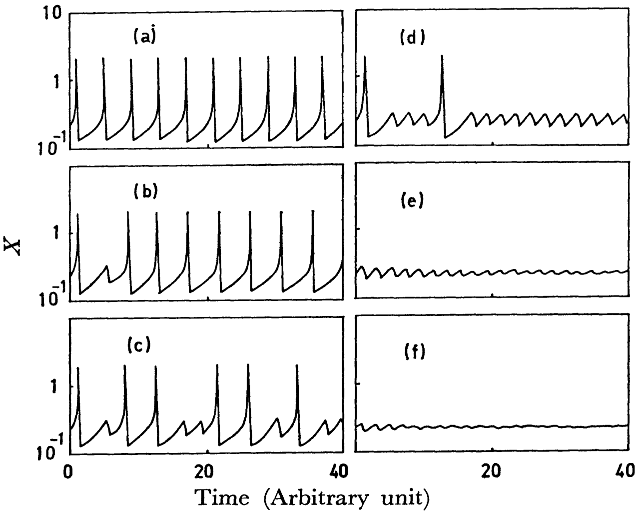

Fig. 8. Oscillatory behaviors under influences of fluctuations. $\beta=J/V$. $\beta'=0.001$, $\gamma=0.001$, $\delta=0.001$, (a) $\beta=0.001$, (b) $\beta=0.006$, (c) $\beta=0.0065$, (d) $\beta=0.007$, (e) $\beta=0.008$, and (f) $\beta=0.01$. $A_0=1.332\times10^5$, $B_0=5.02\times10^5$, $C_0=5.35\times10^5$, $P_0=1.05\times10^5$, $k_1'=0.5\times10^{-5}$, $k_2'=2.38$, $k_3'=1.0\times10^{-3}$, $k_4'=48.64$, $k_5'=1.0\times10^{-4}$, and $k_6'=1.0\times10^{-5}$.

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21) This was confirmed by solving Eqs. 9—14 with a digital computer. The calculated results will appear elsewhere soon.