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Chemical Systems Exhibiting Complicated Temporal Oscillations

Kazutoshi Iwamoto, Susumu Kawauchi, Kiyoshi Sawada, and Manabu Senō*
Institute of Industrial Science, The University of Tokyo, 7-22-1 Roppongi, Minato-ku, Tokyo 106

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Two model systems exhibiting complicated oscillations were proposed and analyzed. One of them is a double oscillation system, which shows alternating oscillations of large and small amplitudes and the mechanism for appearance of the double oscillations is clarified. In the other system, either large or small amplitude oscillation appears depending on the parameter values, and the transition between the large and the small amplitude oscillation is very abrupt and sensitive to the change in external constraints.

Until now, many papers concerning various kinds of behaviors of chemical systems far from equilibrium states have been reported.[1–27] These systems show occasionally some characteristic behaviors like chemical oscillations,[1,2] excitation,[3–5] wave propagation,[6–9] and so on. The well-known chemical oscillatory system is the Belousov-Zhabotinskii reaction,[14,15] in which malonic acid is oxidized by bromate ion catalyzed by some metallic ions in sulfuric acid solutions, and its reaction mechanism has been studied in detail.[16] As a model system for this reaction the Oregonator was proposed and analyzed with a computer simulation method by Field *et al.* of the University of Oregon.[5,17] Similar chemical oscillation models were proposed and analyzed by some investigators.[1–4,18,19] We also proposed a simple model which explains chemical oscillation and excitation,[4] and applied it for interpretation of some problems.[20–23] The characteristic point of the Oregonator and our model is that both of them include a subsystem having multiple steady states, some of which are stable and other are unstable.[4]

In this article, we investigate two chemical systems exhibiting temporal oscillations, one of which shows double oscillation and the other exhibits abrupt changes in the amplitude of oscillation depending on the parameter values.

The former system is obtained by some modifications of our original system[4] and it is useful to investigate the appearance of alternating large and small amplitude oscillations, which are observed in the Belousov-Zhabotinskii reaction in a well-stirred continuous flow reactor.[24,25] A chaotic behavior was also reported in this system.[24] Showalter *et al.* studied a modified Oregonator which exhibits complicated behaviors in a flow system.[26] Although their system, in which two intermediates are newly introduced to the original Oregonator, is fairly complicated, it can well explain the behaviors of the Belousov-Zhabotinskii reaction in the well-stirred continuous flow reactor. A similar model system was studied by Janz *et al.*[27] On the other hand, our system proposed in the present paper contains three intermediates and well explains the appearance of alternating large and small amplitude oscillation.

In the latter system, either large or small amplitude oscillation emerges depending on the parameter values, and the transition between the large and the small amplitude oscillation at critical values of parameters is so abrupt that the system is very sensitive to changes in the external constraints. In this case the behavior of the system at the critical point is largely affected by fluctuations in a similar way as reported already.[3,4,20–22]

Chemical System Exhibiting Double Oscillation

In a preceding paper,[4] we proposed a simple chemical system exhibiting temporal oscillations. Here, the system is modified a little as follows:

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

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

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

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

where the concentrations of A, B, C, P, and R are kept constant to maintain the total system far from an equilibrium state, E and X are intermediates, and Z is a newly introduced chemical species acting as a catalyst in the process (R-1). The chemical species Z is introduced to control the rate of the process (R-1) and for a while its concentration is assumed to be constant.

The rate equations of E and X are written as follows:

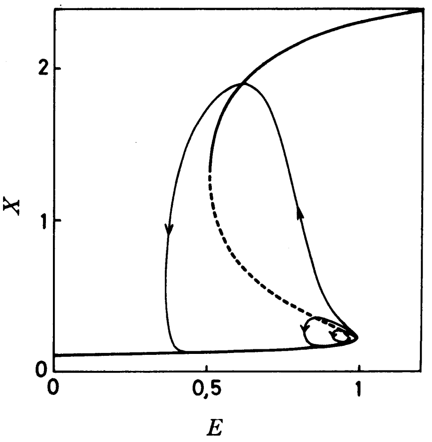

Fig. 1. Phase plane diagrams for Eqs. 3 and 4. Steady states S and S′ are stable and unstable, respectively. The closed cycle shows the trajectory of the temporal oscillation determined by Eqs. 1 and 2 for $Z=1.0$. Parameter values used are: $k_1=1.0$, $k_2=4.76$, $k_3=100.0$, $k_4=48.64$, $k_5=10.0$, $k_6=1.0$, $A=1.332$, $B=5.02$, $C=5.32$, and $P=1.13$.

$$\frac{dE}{dt} = k_1PZ - k_2EX, \tag{1}$$

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

Putting the steady state conditions, $dE/dt=0$ and $dX/dt=0$, into Eqs. 1 and 2 gives

$$k_1PZ - k_2EX = 0, \tag{3}$$

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

By plotting Eqs. 3 and 4 on an E-X phase plane, we get Fig. 1, where two curves from Eq. 3 are shown for $Z=1.0$ and 0.8, respectively. All the parameter values used are as follows:

$$k_1 = 1.0, k_2 = 4.76, k_3 = 100.0, k_4 = 48.64, k_5 = 10.0,$$

$$k_6 = 1.0, A = 1.332, B = 5.02, C = 5.32, \text{and } P = 1.13.$$

The crossing point of the curve of Eq. 3 and that of Eq. 4 represents the steady state of the total chemical system. The steady state indicated with S′, where the value of Z is 1.0, is unstable,[4] and then an oscillatory behavior appears. Its trajectory is shown by a closed cycle in Fig. 1. When the value of Z is 0.8, the crossing point S is a stable steady state, into which the chemical system falls with time independently of the initial states.

Now, let us introduce the following processes.

$$Q \xrightarrow{k_7} Z, \tag{R-5}$$

$$Z + X \xrightarrow{k_8} D + X, \tag{R-6}$$

where the concentrations of Q and D are kept constant. Then, the concentration of Z changes according to the following equation.

$$\frac{dZ}{dt} = k_7Q - k_8XZ. \tag{5}$$

In this equation, the consuming rate of Z, k_8XZ, increases with an increasing concentration of X. When $dZ/dt>0$, that is, the production rate of Z, k_7Q, is larger than the consuming rate of Z, for the system at the state S in Fig. 1, the concentration of Z increases and in time the chemical system will transit towards an oscillatory state. On the other hand, the system in the oscillatory region takes sometimes so large X values during the oscillatory path that the consumption rate of Z increases largely beyond the production rate of Z. Then, the concentration of Z decreases again and the system approaches to the stable steady state showing a damped oscillation.

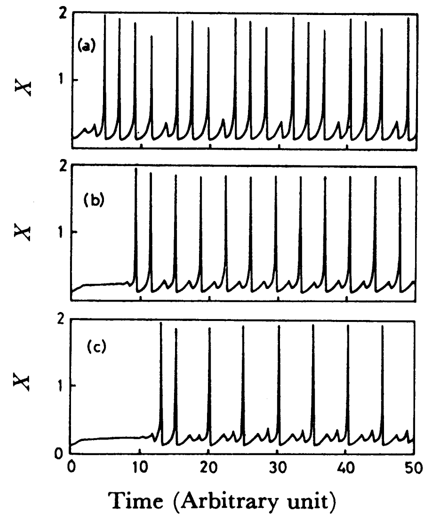

Fig. 2. Some typical behaviors of the double oscillation defined by Eqs. 1, 2, and 5. (a) $P=1.2$, (b) $P=1.13$, (c) $P=1.1$, and $Q=1.0$, $k_7=0.1$, $k_8=0.4$, and other parameter values are the same as those of Fig. 1.

Repetition of these processes causes alternating large and small amplitude oscillations. Figure 2 shows the typical examples of temporal changes of X of the system determined by solving Eqs. 1, 2, and 5 for three values of P. The oscillating behavior changes according to the P value. These results resemble those reported by Hudson *et al.*,[25] although the flow terms are not taken into consideration in the present treatment.

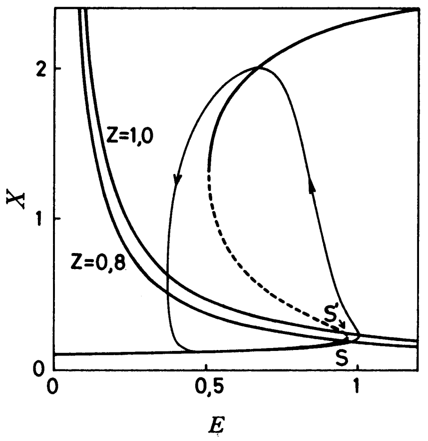

Fig. 3. Projection onto E-X phase plane of the double oscillation trajectory for $P=1.1$. The system evolves from a smallest cycle to a larger and a largest cycles, returning the original smallest amplitude oscillatory state. The parameter values are the same as those of Figs. 1 and 2.

In Fig. 3, the trajectory of oscillation in the case of $P=1.1$ is shown on the E-X phase plane. The thin line representing the trajectory shows that a phase point starts from a certain point on the smallest cycle and transits the phase space into larger cycles, returning to the original small cycle.

Chemical System Showing Abrupt Change in Amplitude

Behaviors of Chemical Reaction Model. Let us consider a system consisting of the following chemical reactions:

$$P' \xrightarrow{pk_9} E', \tag{R-7}$$

$$E' + X' \xrightarrow{pk_{10}} X' + R', \tag{R-8}$$

$$A' + 4X' + E' \underset{k_{12}}{\overset{k_{11}}{\rightleftharpoons}} 5X' + E', \tag{R-9}$$

$$B' + 2X' \underset{k_{14}}{\overset{k_{13}}{\rightleftharpoons}} 3X' + C', \tag{R-10}$$

$$D' + X' \underset{k_{16}}{\overset{k_{15}}{\rightleftharpoons}} G', \tag{R-11}$$

where E' and X' are intermediate species. All the chemical species are represented by superscript dashes to discriminate this chemical system from the double oscillation system described in the preceding section. The concentrations of A', B', C', D', G', P', and R' are kept constant to sustain the system far from an equilibrium state.

The temporal changes of E' and X' are given by

$$\frac{\mathrm{d}E'}{\mathrm{d}t} = \rho k_9 P' - \rho k_{10} E'X', \tag{6}$$

$$\frac{\mathrm{d}X'}{\mathrm{d}t} = k_{11}A'E'X'^4 - k_{12}E'X'^5 + k_{13}B'X'^2 - k_{14}C'X'^3 - k_{15}D'X' + k_{16}G'. \tag{7}$$

At the steady state, where $\mathrm{d}E'/\mathrm{d}t$ and $\mathrm{d}X'/\mathrm{d}t$ are zero,

$$k_9P' - k_{10}E'X' = 0, \tag{8}$$

$$k_{11}A'E'X'^4 - k_{12}E'X'^5 + k_{13}B'X'^2 - k_{14}C'X'^3 - k_{15}D'X' + k_{16}G' = 0. \tag{9}$$

In Fig. 4, Eqs. 8 and 9 are shown on the E-X phase plane for two different values of P'. The parameter values used are:

$A' = B' = C' = D' = G' = 1.0$, $k_9 = 1.0$, $k_{10} = 1.40 \times 10^2$, $k_{11} = 2.5 \times 10^5$, $k_{12} = 5.67 \times 10^5$, $k_{13} = 8.91 \times 10^2$, $k_{14} = 2.50 \times 10^4$, $k_{15} = 12.0$, and $k_{16} = 5.37 \times 10^{-2}$.

The crossing point of the two curves represents the steady state of this chemical system. It was clarified according to the linearized stability analysis1) that the steady state of the chemical system for adequately small ρ values, *e.g.*, smaller than unity, is unstable when the two curves intersect in the dotted parts of the curve drawn by Eq. 9, and in this case we can expect evolution of the system into an oscillatory state.4) The trajectories are dependent on the value of parameter ρ. The closed cycle in Fig. 4 shows approximate path of the temporal oscillation for $P' = 7.90$, where the value of ρ is selected to be 0.01. Dependence of the oscillation behaviors on the position of crossing point is shown in Fig. 5.

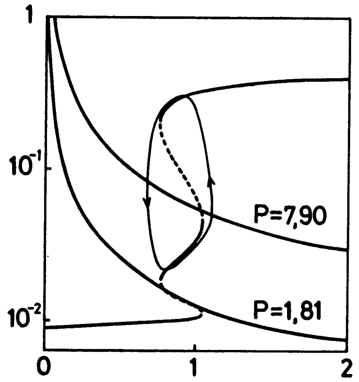

Fig. 4. Phase plane diagrams for Eqs. 8 and 9. The closed cycle is the trajectory of the temporal oscillation determined from Eqs. 6 and 7 in the case of $P' = 7.90$. Parameter values used for calculations are: $A' = B' = C' = D' = G' = 1.0$, $k_9 = 1.0$, $k_{10} = 1.40 \times 10^2$, $k_{11} = 2.5 \times 10^5$, $k_{12} = 5.67 \times 10^5$, $k_{13} = 8.91 \times 10^2$, $k_{14} = 2.50 \times 10^4$, $k_{15} = 12.0$, $k_{16} = 5.37 \times 10^{-2}$, and $\rho = 0.01$.

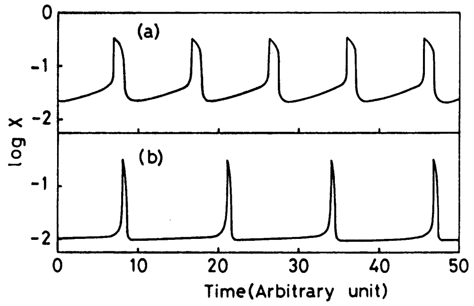

Fig. 5. Oscillatory behaviors of the chemical system. (a) $P' = 7.90$ and (b) $P' = 1.81$. Parameter values used for calculations are the same as those of Fig. 4.

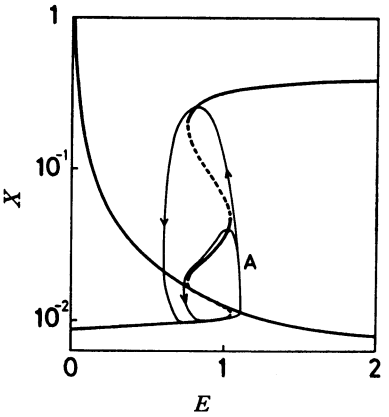

Fig. 6. Trajectories of the oscillations in the case of $P' = 1.81$. Two closed cycles show schematic courses of oscillations for two values, 0.01 and 0.02, of ρ. Point A is a junction at the two cycles. When $\rho = 0.02$, the decreasing rate of E at A is larger than that in the case of $\rho = 0.01$ and the chemical system chooses the course to the small amplitude oscillation.

Next, while the value of P' is fixed to be 1.81, changes in oscillatory behaviors according to the value of ρ is examined. It was revealed that, when ρ is 0.02, the chemical system shows an oscillation of a small amplitude and when ρ is 0.01, an oscillation of a large amplitude appears. Figure 6 shows the approximate trajectories of the chemical system for the two cases of $\rho = 0.01$ and 0.02, respectively. In the case of $\rho = 0.02$, the decreasing rate of E at the junction A at the two passes is faster than that in the case of $\rho = 0.01$ and, therefore, the chemical system chooses the course of the small cycle. Both the oscillatory behaviors are shown in Fig. 7. The larger amplitude oscillation has longer period than that of the smaller amplitude oscillation. The abrupt change in amplitude is observed between 0.019 and 0.018 of ρ value, and for ρ values larger than 0.019, the smaller amplitude oscillation appears.

The characteristic point of the present chemical system is that the amplitude of oscillations changes largely at a certain value of ρ, and we can say that this system is very sensitive to change of parameter values.

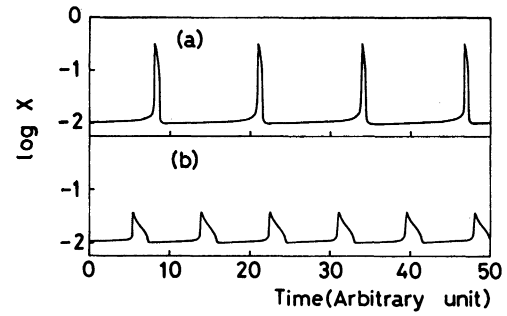

Fig. 7. Oscillatory behaviors of the chemical system for $P'=1.81$. (a) $\rho=0.01$ and (b) $\rho=0.02$. Other parameter values are the same as those of Fig. 5. The critical value of ρ, at which the amplitude changes abruptly, is between 0.018 and 0.019.

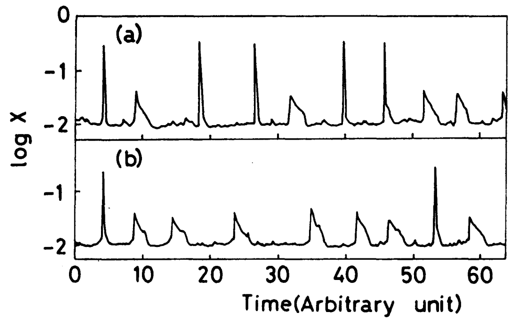

Fig. 8. Appearance of random oscillations in amplitude under the influence of fluctuation. $P'=1.81$. (a) $\rho=0.018$ and (b) $\rho=0.019$. The strengths of fluctuations are selected to be $\alpha=0$ and $\beta=0.1$ for calculations. Other parameter values are the same as those of Fig. 5.

Effects of Fluctuations on the Behaviors of the Chemical System. Since the chemical system described in this section is very sensitive to a small variation in the parameter values, it would be expected that the amplitude of oscillations of this chemical system changes randomly under the influence of fluctuation. To confirm this expectation, the following Langevin type equations representing the behaviors of the chemical system subjected to fluctuation should be examined; that is,

$$\frac{\mathrm{d}E'}{\mathrm{d}t} = \rho k_9 P' - \rho k_{10} E'X' + \alpha F(t), \tag{10}$$

$$\frac{\mathrm{d}X'}{\mathrm{d}t} = k_{11}A'E'X'^4 - k_{12}E'X'^5 + k_{13}B'X'^2 - k_{14}C'X'^3$$
$$-k_{15}D'X' + k_{16}G' + \beta H(t), \tag{11}$$

where $F(t)$ and $H(t)$ are the fluctuation terms of Gaussian type. The average values $\langle F(t)\rangle$ and $\langle H(t)\rangle$ are zero and the standard deviations are set to be 0.1. The coefficients α and β represent the strengths of fluctuations. Figure 8 illustrates typical behaviors of the chemical system under the influence of fluctuations, which were obtained by solving these equations in some cases. Certainly, random appearance of large and small amplitude oscillations is observed.

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