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The Number of Autocatalytic Reactions in Systems of Oscillating Reaction

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Abstract. Some mathematical models have been proposed to elucidate the mechanism by which an oscillating reaction is generated as a complex system. Brusselator and Oregonator do not only describe oscillating reaction systems but also reproduce multiple periodic oscillations, burst waves and drawing synchronization. All theoretical researches on these models did not give each differential equation with consideration of the strict correspondence to the system of reactions. Then, we did not adopt a theoretical framework of physics but a mathematical one in which it is possible to survey exhaustively although most of the elements might look apart from real chemical systems. We have been interested in the problem of the least number of chemical species and elementary reactions that can generate the reaction. In this study, we mainly analyzed two chemical species that are not supplied continuously in *Continuous-flow Stirred Tank Reactor* (*CSTR*). We have demonstrated that the *oscillating reaction systems* must be described by more than one reaction formula that contains formulae for the *autocatalytic reactions* with physical consideration of the *equilibrium space* of its rate equations. We have contemplated the mathematical meaning of the *autocatalytic reaction* and showed that a positive feedback system gives it; therefore, an *oscillating reaction* can be produced by a complex feedback system.

1. Introduction

In reaction kinetics, a reaction in which the concentration of the components in the system changes periodically as the reaction progresses is called an oscillating reaction. The Bray-Liebhafsky reaction (BRAY, 1921) and some oscillating reactions have been identified experimentally (LEHNINGER *et al.*, 1993). However, it is difficult to classify most of these systems of reactions into minimal elements. For example, the Belousov-Zhabotinsky (BZ) reaction is generated by a Ce ion-malonic acid-bromic acid system. It is believed that more than 10 reactants are contained in the system of reactions, including intermediate products such as malonic acid, bromic acid, Ce^{3+}, Ce^{4+}, bromo-malonic acid, bromous acid, bromous acid radical, hypobromous acid, bromine and bromine ion (TYSON, 1985). They have minutely studied elementary reactions that compose the BZ reaction and calculated their rate constants. A typical reaction is the FKN mechanism (FIELD *et al.*, 1972) that is summarized as 10 elementary reactions. However, there are many points of uncertainty, for example admission of the radical reaction, Fe(IV) ions, and the reactions involving organic compounds. These mechanisms have been modified in many studies (YAMAGUCHI, 1991). The BZ reaction is known as a complex system that consists of multiple elementary reactions.

It is difficult for a reaction formula to describe the system of the BZ reaction as an oscillating reaction. Many studies have examined the elementary reactions that compose systems of the oscillating reaction, and systems of differential equations have been devised as models for the generation of chemical oscillation. More than 60 models have been proposed to describe the oscillating reactions systems (YAMAGUCHI, 1991). The Lotka-Volterra model (LOTKA, 1920) is one of them, which corresponds to a system of irreversible reactions in an open system;

$$\begin{aligned} &A + X \xrightarrow{\alpha} 2X \\ &X + Y \xrightarrow{\beta} 2Y \\ &Y \xrightarrow{\gamma} E \end{aligned} \tag{1}$$

where the concentration of reactor A is assumed to be constant. The substrate A reacts on the intermediate X and changes to X, and X reacts to the intermediate Y and changes to Y. The products X, Y react as catalysts in each reaction. We can regard these reactions as processes for auto-duplication of those catalysis. The process accompanying this autocatalysis is called an autocatalytic reaction.

Previous studies have proposed that the oscillating reaction system involves both an autocatalytic process and a feedback control process (BLANDAMER, 1975). According to the method predicated on elementary reactions (HORIUCHI, 1956), TAKADA and KITAOKA (2001) composed a first-order simultaneous system of differential equations as a system of rate equations for all concentration variables of species in the system of elementary reactions. They proved two mathematical theorems to demonstrate the necessity of these processes in some conditions. Although their study might focus onto a system of the mathematical models regardless of the reality for reaction systems, their models covered real chemical reactions thoroughly so that complex systems also came into view. Moreover, it seems to be important to examine the role of mathematical models in chemical reaction kinetics exhaustively because the models are relatively easy to deal with from the point of view of exotic phenomena, the qualitative theory of differential equations in general, and catastrophe theory in particular. Our work is also one of the mathematical studies. Although we use the mathematical word "equilibrium" in this paper below, its meaning is different from "equilibrium" on thermodynamics as mentioned in the beginning of Appendix.

Definition Let a phase space to be $\mathbf{R}^n$, and smooth functions to be f_j ($j = 1, 2, ..., n$). A simultaneous system of differential equations for variables $x_1, x_2, ..., x_n \in \mathbf{R}^n$:

$$\frac{dx_j}{dt} = f_j \left(x_1, x_2, \ldots, x_n\right) \left(j = 1, 2, \ldots, n\right) \tag{2}$$

controls a representation point $\vec{x} = (x_1, x_2, ..., x_n)$, and defines flow in the phase space $\mathbf{R}^n$. I assume zero points of this flow $d\vec{x}/dt = 0$ to be equilibrium points.

The equilibrium points construct an equilibrium space $f_1(\vec{x}) = f_2(\vec{x}) = \cdots = f_n(\vec{x}) = 0$. An equilibrium space for the variable x_j consists of points that satisfy $f_j(\vec{x}) = 0$. The flow on this space is static in the direction of x_j on the account of Eq. (2). Thus, the representation point would stop in a direction of x_j if it attained the equilibrium space for the variable x_j. However, this space does not guarantee stability in the other directions.

In this paper, we also conform to their scheme (Appendix). We review our physical consideration as follows, and give an expression for the process as a feedback system.

1. We must compose multiple elementary reaction formulae as an oscillating reaction system according to an analytical solution of the system of rate equations.
2. The oscillating reaction system involves one or more autocatalytic process in Continuous-flow Stirred Tank Reactor (CSTR).

CSTR is used as the reaction container, and it satisfies the conditions of an open system. Some concentrations of the elements are maintained constant in the container with external supply of solutions such as malonic acid, bromic acid ion, and hydrogen ion solutions. Moreover, we can apply external periodic perturbations, and the CSTR enables strict analysis of oscillating reactions such as the BZ reaction, which seems to be generated by a chaos system (DOLNÍC *et al.*, 1989; NOSZTICZIUS *et al.*, 1989).

After the review, we show that a positive feedback system cannot produce the oscillating reaction, and the reaction system involves multiple positive feedback systems.

2. Historical

TAKADA and KITAOKA (2001) proved two theorems for dynamical consideration of an autocatalytic reaction in systems of the oscillating reaction. Here, we give those theorems and review their clime on the autocatalytic reaction. We also provide a dynamical interpretation of the necessity of an autocatalytic reaction in systems of the oscillating reaction, which is based on those mathematical theorems.

2.1. Theorems

One of those theorems was a theoretical suggestion that a certain equilibrium state was reached for any initial conditions if the reaction system could be described by a reaction formula. Herein, we define the restricted phase space by a half-interval $\mathbf{R}_+ = \{x | x \geq 0, x \in \mathbf{R}\}$ on any variables where $\mathbf{R}$ is a set of all real numbers. It corresponds to those concentration variables that give positive values.

Theorem 1 Let coefficients α, β, a_i, b_j be positive values ($i = 1, ..., n$; $j = 1, ..., m$) and $q \in \mathbf{N}$ (natural number). In restricted phase space spanned by variables $x_1, ..., x_n, y_1, ..., y_m, z \in \mathbf{R}_+$ that compose a simultaneous system of differential equations with $(m + n + 1)$ unknowns, a solution of

$$\begin{cases} \dot{x}_i / a_i = -\left(\alpha z^q \prod_{k=1}^{n} x_k^{a_k} - \beta z^{q+1} \prod_{l=1}^{m} y_l^{b_l}\right) & ; \quad i = 1, 2, \ldots, n \qquad (3) \\ \dot{y}_j / b_j = z^q \prod_{k=1}^{n} x_k^{a_k} - \beta z^{q+1} \prod_{l=1}^{m} y_l^{b_l} & ; \quad j = 1, 2, \ldots, m \qquad (4) \\ \dot{z} = \alpha z^q \prod_{k=1}^{n} x_k^{a_k} - \beta z^{q+1} \prod_{l=1}^{m} y_l^{b_l} & \equiv \quad z^q (A - B) \qquad (5) \end{cases}$$

asymptotically and monotonously converges for any initial values.

We have shown that a solution of the system of rate equations (3)–(5) monotonously converges on an equilibrium point for all initial values in accordance with Theorem 1. Here the monotone means that a first differential with respect to each concentration variable $\dot{x}_1$, ..., $\dot{x}_n$, $\dot{y}_1$, ..., $\dot{y}_m$, $\dot{z}$ gives a constant sign along each orbit as a solution. We could also understand that the equilibrium space $z = 0$ was a set of singular points that did not give minimal points of the potential function for a representation point in the phase space $\mathbf{R}_+^{n+m+1}$. Thus, we concluded that the equilibrium space $z = 0$ was not stable.

We have also proved the other theorem on a manifold as the equilibrium space as follows. This is theoretical evidence that it is impossible for any pair of densities for non-provided chemical species to oscillate in CSTR without any autocatalysis.

Theorem 2 The following algebraic curve $L(y, x) = 0$ is univalent for y on $y, x \in \mathbf{R}_+$.

$$L(y, x) \equiv -u(y, x) - v(y) + \phi(x) = 0 \qquad (6)$$

$$\begin{aligned} s.t. \quad & u(y, x) \equiv \sum_{k,l>0} a_{kl} y^k x^l, \quad v(y) \equiv \sum_{k>0} a_{k0} y^k, \quad \phi(x) \equiv \sum_{l \geq 0} a_{0l} x^l, \\ & \forall k, l \in \mathbf{R}_+; \quad a_{kl} > 0. \end{aligned} \qquad (7)$$

2.2. Dynamical interpretation of Theorem 1

Let the reactants be X_1, ..., X_n, products Y_1, ..., Y_m and an autocatalytic specie Z. Concentration variables of all chemical species in a reaction formula

$$a_1 X_1 + \cdots + a_n X_n + qZ \underset{\beta}{\overset{\alpha}{\rightleftarrows}} b_1 Y_1 + \cdots + b_m Y_m + (q+1)Z \qquad (8)$$

with auto-catalysis could be described by the rate equation system (3)–(5) under a definition of rate equations in the Appendix ($q \in \mathbf{N}$). If an initial condition was $z = 0$, the reaction formula (8) would not contain autocatalytic species and this reaction formula could describe a general reaction without autocatalysis.

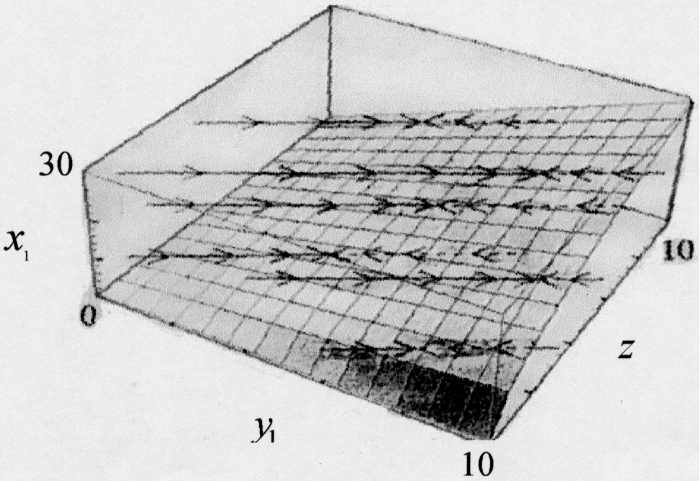

Fig. 1. This figure presents an example of the equilibrium space $A - B = 0$ and the trajectory of solutions for differential equations (3)–(5) with the conditions of $m = n = 1$, $\alpha = \beta$ and $a_1 = b_1 = 2$.

Theorem 1 offered a dynamical analysis of the system of rate equations (3)–(5). We developed this theorem for asymptotical monotone convergence of the representation point controlled by the system of equations. Solutions for the system of differential equations (3)–(5) did not form a periodical variation for any components, and they asymptotically converged on a point in the equilibrium space (Fig. 1).

A concentration of the components changes periodically in systems of the oscillating reaction. We could distinguish whether the system of rate equations described the oscillating reaction system by an analysis of the existence of the periodical solution for the system of differential equations. Theorem 1 showed that no component in a solution for the system of rate equations formed a periodical variation without autocatalysis. Therefore, we could suggest that an oscillating reaction was not produced by an elementary reaction. We believe that the oscillating reaction requires a system of reactions that contains more than one elementary reaction. Actuary, some reaction systems are known as mechanisms to generate the oscillating reaction, that are composed of plural elementary reactions such as Brusselator (BLANDAMER and MORRIS, 1975) and Oregonator (TYSON, 1985).

Based on the above, in the next chapter we consider a system of rate equations composed of plural reaction formulae without autocatalysis.

2.3. Dynamical interpretation of Theorem 2

One of oscillating reactions is the BZ reaction. It is generated by a mixture of four inorganic substances. We can observe that the mixture takes on blue and red colors periodically and alternatively. It derives from a particular material (an iron ion) that changes between two states (YOSHIKAWA, 1992). Similarly, for Theorem 2 we have assumed that more than one concentration variable changes between two states periodically in phase space spanned by all concentration variables in the oscillating reaction system.

Specifically, we have assumed that the representation point for the system of rate equations is in the same state only if it belongs to a stable, simply connected equilibrium space in the phase space that is composed of all concentration variables x_1, ..., x_n ($\in \mathbf{R}_+$), and it periodically moves between two spaces in the oscillating reaction system. We then make the following assumption:

Assumption 1 Any concentration variable in the system of rate equations periodically changes with the transition of the representation point between two stable equilibrium spaces that are not simply connected, which describes the oscillating reaction system.

We noted the number of stable equilibrium spaces that are not simply connected in order to examine the transition between two stable equilibrium spaces, and analyzed the "form of the equilibrium space". However, it is generally difficult to analyze the structure of the equilibrium space for n-variables in phase space $\mathbf{R}_+{}^n$. Here, we analyze the structure of the two-dimensional cross section that is defined by all pairs of concentration variables with the assumption of continuity of the equilibrium space.

Assumption 2 Let any pair of concentration variables for chemical species be variable, and the others be adiabatic constants.

This assumption corresponds to an analysis on variation process for any pair of chemical species that is not provided continuously into CSTR without an autocatalytic reaction.

In a reaction system composed of more than one elementary reaction formula without autocatalysis, an equilibrium space $\dot{x}_j = 0$ for concentration variables x_j of chemical species X_j ($j = 1, ..., n$) is given as

$$\sum_{k=1}^{N} m_{kj}\left(-\alpha_k \prod_{l\in\nu_k(j)} x_l^{m_{kl}} + \beta_k \prod_{l\in\nu_k(j)} x_l^{m_{kl}}\right) = 0 \tag{9}$$

by Eqs. (A.1), (A.2) and Appendix. If we observed any pair of concentration variables x_i, x_j ($i \neq j$), we could describe a two-dimensional cross section of the equilibrium space as Eq. (6), assuming $x_i \equiv x$, and $x_j \equiv y$. That is, Eq. (6) expresses the two-dimensional cross section of the equilibrium space for a concentration variable of the chemical species Y without autocatalytic species. We compared these cross sections with the equilibrium space

$$\alpha z^q \prod_{k=1}^{n} x_k^{a_k} - \beta z^{q+1} \prod_{l=1}^{m} y_l^{b_l} = 0, \tag{10}$$

with the concentration variable of an autocatalytic specie in Eq. (8). Although all coefficients for the variable x_j (=y) in Eq. (6) were negative, positive coefficients were added in Eq. (10). Then, we could believe that the autocatalytic reaction gives the following mathematical effects.

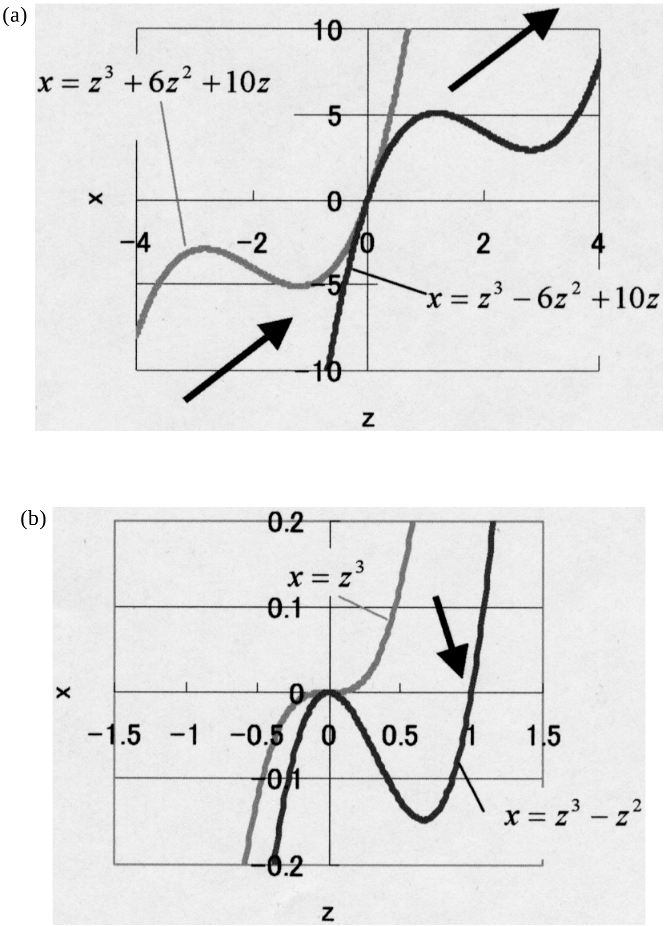

Fig. 2. These figures show two-dimensional cross sections of the equilibrium spaces (11). (a) This figure consists of algebraic curves $F(z, x) = 0$ with the condition of $u = 0$, $v = z^3 + 6z + 10z$, $w = x$, and with $u = 12z^2$, $v = z^3 + 6z + 10z$, $w = x$. (b) This figure consists of algebraic curves $F(z, x) = 0$ with the condition of $u = 0$, $v = z^3$, $w = x$, and with $u = z^2$, $v = z^3$, $w = x$.

1) A parallel transfer of the orbit closure to positive region in phase space (Fig. 2(a))

2) Multi-valued algebraic curves for the variable with non-degenerate singular points (Fig. 2(b)).

Otherwise, two-dimensional cross sections (6) for any variables on the equilibrium space ($\subset \mathbf{R}_+{}^n$) were univalent in accordance with Theorem 2. Hence, there were not two or more stable partial equilibrium spaces that were not simply connected. The system of rate equations without autocatalysis did not have a periodic solution with transition between two stable equilibrium spaces under Assumption 1–2. We conclude that no pair of densities for non-provided chemical species changes periodically in a CSTR that has no autocatalytic reaction. It is suggested theoretically that an oscillating reaction is not generated by those reaction systems.

3. Our Proposition

We give an original proposition as an expansion of Theorem 2. This proposition also gives a single-valued manifold as the equilibrium space. This is theoretical evidence that no pair of densities for non-provided chemical species can oscillate in CSTR with an autocatalytic reaction.

3.1. Propositions

The following theorem on analytics was useful in proving that a graph of two monotonous functions with different signs of derivation intersects in a bounded closed interval.

Intermediate value theorem A function $f \in \mathbf{C}^0[s_1, s_2]$ with $f(a) \neq f(b)$ gives all values between $f(a)$ and $f(b)$.

The following Proposition was obtained by this theorem. Our proposition provides theoretical evidence that no pair of non-provided chemical species produces an oscillating reaction in CSTR with an autocatalytic reaction.

Proposition The algebraic curve $F(z, x) = 0$ is univalent for z on $z, x \in \mathbf{R}_+$.

$$\begin{aligned} &F(z,x) \equiv -u(z,x) - v(z) + w(x) + \phi(x)z^q - \psi(x)z^{q+1} = 0 \\ &s.t. \quad u(z,x) \equiv \sum_{k,l>0} a_{kl} z^k x^l, \quad v(z) \equiv \sum_{k>0} a_{k0} z^k, \quad w(x) \equiv \sum_{l \geq 0} a_{0l} x^l \end{aligned} \tag{11}$$

$$\begin{aligned} &\phi(x) \equiv b_1^- x^m + b_0^-, \quad \psi(x) \equiv b_1^+ x^n + b_0^+ \\ &\forall k, l \in \mathbf{R}_+: \ a_{kl} > 0, \ b_1^{\pm} \geq 0. \end{aligned} \tag{12}$$

3.2. Proof for our proposition

We choose any real number $\zeta \in \mathbf{R}_+$. The number of intersections between $x = \zeta$ and the algebraic curve $F(z, x) = 0$ agrees with the number of solutions to the algebraic equation $F_\zeta(z) \equiv -F(z, \zeta) = 0$. The number of solutions to this equation also agrees with the number of intersections between the curve $w = F_\zeta(z)$ and the line $w = 0$.

Now we define

$$e_1 \equiv \sum_{l \geq 0} a_{0l} \zeta^l, \quad e_2(k) \equiv \sum_{l \geq 0} a_{kl} \zeta^l \tag{13}$$

where e_1 and $e_2(k)$ are positively definite for any k because of condition (12) and $\zeta \in \mathbf{R}_+$.

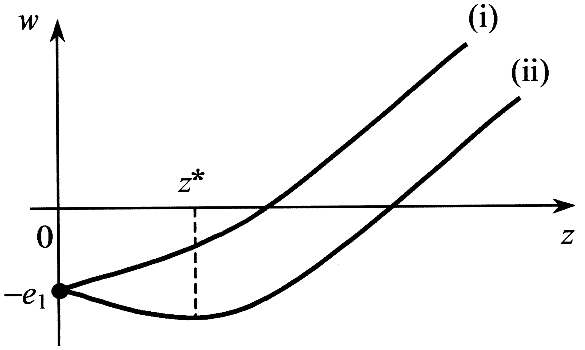

Fig. 3. This figure presents the graph of $w = F_\zeta(z)$ with the condition of $\mathrm{I}(z) > |\mathrm{II}(z)|$ for any $z \le q(b_1^- \zeta^n + b_0^-)/(q+1)(b_1^+ \zeta^m + b_0^+)$ (the curve (i)) and $\mathrm{I}(z) \le |\mathrm{II}(z)|$ for any $z < z^* \le q(b_1^- \zeta^n + b_0^-)/(q+1)(b_1^+ \zeta^m + b_0^+)$ (the curve (ii) where z^* is the minimal point for this algebraic curve. This value is given by the solution to the equation $\mathrm{I}(z) + \mathrm{II}(z) = 0$.

The $F_\zeta(z)$ can be rewritten with the constant e_1 as

$$\begin{aligned} F_\zeta(z) &= \sum_{k,l>0} a_{kl}\zeta^l z^k + \sum_{k>0} a_{k0} z^k - \sum_{l\ge 0} a_{0l}\zeta^l + \left(b_1^+\zeta^m + b_0^+\right)z^{q+1} - \left(b_1^-\zeta^n + b_0^-\right)z^q \\ &= \sum_{k>0}\left(\sum_{l\ge 0} a_{kl}\zeta^l\right)z^k - e_1 + z^q\left\{\left(b_1^+\zeta^m + b_0^+\right)z - \left(b_1^-\zeta^n + b_0^-\right)\right\}. \end{aligned} \tag{14}$$

If z were equal to 0, the polynomial $F_\zeta(z)$ would have a negative sign; that is, $F_\zeta(z) = -e_1 \le 0$. A partial derivation of the polynomial $F_\zeta(z)$ is the following expression.

$$\frac{\partial F_\zeta(z)}{\partial z} = \sum_{k>0} e_2(k)kz^{k-1} + z^{q-1}\left\{(q+1)\left(b_1^+\zeta^m + b_0^+\right)z - \left(b_1^-\zeta^n + b_0^-\right)\right\} \equiv I(z) + II(z). \tag{15}$$

(i) If the first term on the right side of Eq. (15) is more than the absolute value of the second term $\mathrm{I}(z) > |\mathrm{II}(z)|$ for any $z \le q(b_1^- \zeta^n + b_0^-)/(q+1)(b_1^+ \zeta^m + b_0^+)$, this partial derivation is a positive value because of the inequality of the coefficient at the first term $ke_2(k) > 0$, of the coefficient at the second term $(b_1^+ \zeta^m + b_0^+) > 0$ and $z \in \mathbf{R}_+$. In this case, $F_\zeta(z)$ is a strictly monotonous and increasing function; that is, the curve $w = F_\zeta(z)$ increases monotonously (Fig. 3). The function $F_\zeta(z)$ diverts as z goes to infinity because the coefficients for z on the polynomial (14) are positive. The function $F_\zeta(z)$ is one of the elements that belong to the set of continuous functions $\mathbf{C}^0[0, \infty)$; therefore, the curve $w = F_\zeta(z)$ and the line $w = 0$ intersect at one point in accordance with the intermediate value theorem.

(ii) If the first term on the right side of Eq. (15) is not more than the absolute value of the second term $\mathrm{I}(z) \le |\mathrm{II}(z)|$ for any $z < z^* \le q(b_1^- \zeta^n + b_0^-)/(q+1)(b_1^+ \zeta^m + b_0^+)$, the partial derivation is negative for the interval $[0, z^*)$ and positive for any $z \geq z^*$ because the polynomial $\mathrm{II}(z)/z^q$ is linear (Fig. 3).

First of all, $F_\zeta(z)$ is a strictly monotonous and decreasing function in the interval $[0, z^*)$. Thus, the curve $w = F_\zeta(z)$ decreases monotonously for this interval. Then, the function $F_\zeta(z)$ gives the minimum value at the right end of this interval $z = z^*$. Thus, the procedure for both ends of this interval is $(0 \geq e_1 =)F_\zeta(0) > F_\zeta(z^*)$. The function $F_\zeta(z)$ is one of the elements that belong to the set of continuous functions $\mathbf{C}^0[0, z^*)$; therefore, this function does not give zero value in accordance with the intermediate value theorem. The curve $w = F_\zeta(z)$ and the line $w = 0$ do not intersect at any point in the interval $(0, z^*)$.

In the other interval on $z \in \mathbf{R}_+$, $F_\zeta(z)$ is a strictly monotonous and increasing function. That is, the curve $w = F_\zeta(z)$ increases monotonously for any $z \geq z^*$. The function $F_\zeta(z)$ gives $F_\zeta(z^*) < 0 < \lim_{z \to \infty} F_\zeta(z) = \infty$ at boundaries of this interval $[z^*, \infty)$. The function $F_\zeta(z)$ is one of elements that belong to the set of continuous functions $\mathbf{C}^0[z^*, \infty)$; therefore the curve $w = F_\zeta(z)$ and the line $w = 0$ intersect at one point for the interval (z^*, ∞) in accordance with the intermediate value theorem.

In either event, the curve $w = F_\zeta(z)$ and the line $w = 0$ intersect at one point for $z \in \mathbf{R}_+$. There is a solution to the equation $F_\zeta(z) = 0$, so the algebraic curve $F(z, x) = 0$ is univalent for z on $z, x \in \mathbf{R}_+$. [Q.E.D.]

4. Discussion

4.1. Dynamical interpretation of our proposition

TAKADA and KITAOKA (2001) have claimed that it is possible for the autocatalytic reaction formula in a system of reaction formulae to describe the oscillating reaction system with the theorems mentioned above and their theoretical considerations (Table 1). Actuary, the chemical oscillation could be described by solutions for some of the rate equations such as Lotka-Volterra systems if there were autocatalytic reaction formulae in a system of plural reaction formulae (SAITOH, 1998).

We were cautious in considering the origin of the oscillating reaction. We strictly studied the conditions under which there were oscillating reaction systems in Table 1. There is more than one autocatalytic reaction formula in the system of reaction formulae,

Table 1. This table indicates conditions to describe the chemical oscillations. We can generate periodic solutions for systems of rate equations with the condition marked "○" and vice versa. Proposed mathematical models for the chemical oscillations had the condition marked "○". We considered Theorem 1 and Theorem 2 to be evidence for the conditions marked "×".

Existence of autocatalytic reaction in the reaction formulae	The number of reaction formulae	
	1	2 or more
In their absence	×	×
Exist	×	○

as in the examples mentioned above. We posed the question of the smallest number of autocatalytic reaction formulae that could generate the oscillating reaction.

We also analyzed the variation process for any pair of chemical species, which was not provided continuously into the CSTR. We considered the concentrations of any pair of chemical species to be variable, and others to be adiabatic, as in Assumption 2. Our proposition showed the structure of any two-dimensional cross section that was defined by all pairs of concentration variables in the reaction system with an autocatalytic reaction formula.

We could consider any equilibrium space $\dot{x}_j = 0$ for a concentration variable to be Eq. (9) if we observed an ordinal system of reactions without the autocatalytic species, which was composed of two or more elementary reactions ($\forall j \in \mathbf{N}$). A two-dimensional cross section of this equilibrium space was described by $L(y, x) = 0$ with the assumption of $x_i \equiv x$ and $x_j \equiv y$. However, if we observed a system of reactions with the autocatalytic specie Z, the equilibrium space on the concentration valuable z should be given as

$$\alpha z^q \prod_{l \in v_0(j)} x_l^{m_{0l}} - \beta z^{q+1} \underline{\prod}_{l \in v_0(j)} x_l^{m_{0l}} + \sum_{k=1}^{N} m_{kj} \left(-\alpha_k \prod_{l \in v_k(j)} x_l^{m_{kl}} + \beta_k \underline{\prod}_{l \in v_k(j)} x_l^{m_{kl}} \right) = 0 \qquad (16)$$

by Eqs. (A.1) and (A.2), because there were no autocatalytic species except for Z. A two-dimensional cross section of this equilibrium space was described by $F(z, x) = 0$ with the assumption of $x_j \equiv z$, and $x_i \equiv x$ which was not a concentration variable for the autocatalytic specie. Comparing the algebraic curve $F(z, x) = 0$ with $L(y, x) = 0$, the former (11) had different signs of the coefficient for the first variable. The first term in Eq. (16) gave Eq. (11) the positive term $\phi(x)z^q$ for the first variable, although all coefficients in Eq. (6) were negative. There were non-degenerate singular points along the algebraic curve $F(z, x) = 0$, and this curve was univalent in the phase space $\mathbf{R}_+{}^n$ according to our proposition. There were no plural stable partial equilibrium spaces that were not simply connected, and the representation point could not move between two stable equilibrium spaces under Assumption 1–2. We believe that there are no orbit closures in the phase space $\mathbf{R}_+{}^n$, and it is impossible to generate periodic solutions of the systems of rate equations for an autocatalytic reaction and other elementary reactions. In the CSTR that has an autocatalytic reaction, we concluded that no pair of densities for non-provided chemical species changes periodically. It was suggested theoretically that an oscillating reaction was not generated by this reaction system.

Thus, there is little probability that the oscillating reaction is caused by a system of reaction formulae with an autocatalytic reaction formula. We believe that it is necessary to possess two or more autocatalytic reactions in the system of reactions so as to generate the oscillating reaction.

4.2. Autocatalytic reaction as a positive feedback system

In Subsec. 2.3, we induced that a system of the oscillating reaction involves an autocatalytic reaction with physical assumptions that limit the system of reactions. Here, we consider and express the mathematical meaning of the autocatalytic reaction.

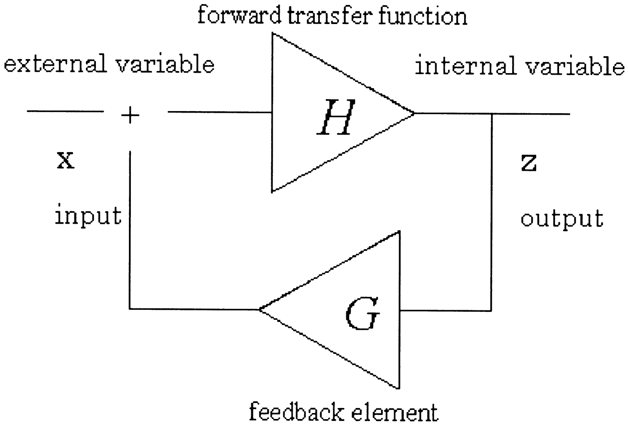

Fig. 4. This block diagram describes the relationship between input and output of the positive-feedback systems.

According to the rate equation (3)–(5), we showed the equilibrium space for a concentration variable of the autocatalytic specie Z in the chemical reaction (8) as Eq. (10), whereas the autocatalytic reaction was a production process of the autocatalytic specie as described in the introduction. The production of the autocatalytic process advances by itself. Such a process is often described as a positive-feedback system (MORI and NAKATA, 1994).

In engineering, positive-feedback systems have been described by block diagrams as in Fig. 4, where the variable x is an input (external) variable, z is an output (internal) variable, H is a forward transfer function and G is a feedback element. These systems were also expressed by the following functional equation:

$$H(x + G(z)) = z \quad \text{i.e. } x = (H^{-1} - G)(z). \tag{17}$$

We have supposed that the relation between the input and output is satisfied by dynamical equilibrium for the system of differential equations, which describes the positive-feedback process, only when we assumed the forward transfer function to be $H(z)$ and the feedback element $G(z)$, where

$$H(z) = \left(\frac{z}{\alpha \prod_{k=1}^{n} x_k^{a_k}} \right)^{1/q}, \quad G(z) = \beta z^{q+1} \prod_{l=1}^{m} y_l^{b_l}. \tag{18}$$

In accordance with Eq. (17), the equilibrium space of the process should be

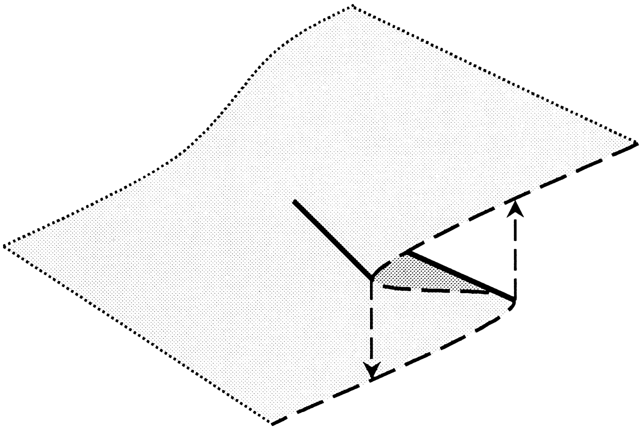

Fig. 5. This figure shows the Riemann-Hugoniot manifold. The representation point moves along the cross section of this manifold, which is controlled by van der Pol equations (VAN DER POL, 1926), particular Liènard equations. The point jumps into another subspace if it reaches an unstable equilibrium point, the edge of the manifold (thick lines).

$$\begin{aligned} x &= \alpha z^{q}\prod_{k=1}^{n} x_k^{a_k} - \beta z^{q+1}\prod_{l=1}^{m} y_l^{b_l} \\ &= z^{q}\left[\alpha\prod_{k=1}^{n} x_k^{a_k} - \beta z\prod_{l=1}^{m} y_l^{b_l}\right]. \end{aligned} \tag{19}$$

This equilibrium space is homomorphic to the Riemann-Hugoniot manifold (POSTON and STEWART, 1978) on the condition of $q = 2$ (Fig. 5). Equation (10) was also obtained by the restriction of this equilibrium space as $x = 0$. The equilibrium space for the concentration variable of an autocatalytic specie fit a subspace of the equilibrium space for an internal variable in the feedback system. The autocatalytic reaction should be described by a positive-feedback system mathematically if we assume one output variable in the system to be the internal variable in differential equations that describe the system and construct the equilibrium space for the variable with the relation between input and output of the system.

In this paper, we have also made the theoretical suggestion that an oscillating reaction is not produced by a system of reactions with an autocatalytic reaction, but by plural autocatalytic reactions. Thus, a system of the oscillating reaction must be given by a complex system consisting of the positive feedback processes. We believe that it will be useful henceforth to transform the figure of networks (the block diagram) into the system of differential equations. In contrast, we can obtain the dynamical system as the mathematical model from the diagram.

The other side, we also showed evidence that the oscillating reaction could not be given by reaction systems with an autocatalytic reaction formula as a positive feedback system, which was our claim in this paper. We introduced the retardant time on block diagrams for the feedback system and set a new expression for time variations by the output of the system. We obtained differential equations that were induced by the expression of time variations for input and outputs of the feedback systems with retardant time on some definitions and assumptions (TAKADA *et al.*, 2000). Family of the Liènard equation (HIRSCH and SMALE, 1974) contained the differential equations that were induced by the expression for negative feedback systems with retardant time although the family did not contain the differential equation for positive feedback systems. These are non-linear differential equations. The former deferential equations generate orbit closures on the phase plane in the large. LEFSCHETZ (1946) proved that the Liènard equation has a periodic solution with his geometrical consideration. The solution for the later differential equations diverged to infinity with qualitative consideration of vector field produced by the differential equations. We also concluded that the oscillating reaction system could not be described by the reaction system with an autocatalytic reaction formula as a positive feedback system.

5. Conclusion

We composed a system of rate equations for concentration variables of all kinds of chemical species in the system of reaction formulae. We have solved the system of differential equations and concluded that an elementary reaction could not generate the oscillating reaction. We have analyzed the structure of the equilibrium space for the system of rate equations, which describes a system of reversible reaction formulae without autocatalysis. In this system of reaction formulae, we have concluded that the oscillating reaction is not caused by concentrations for any pair of species that are not supplied continuously into the Continuous-flow Stirred Tank Reactor (CSTR). We have also analyzed the structure of the equilibrium space for the system of rate equations, which describes a system of reversible reaction formulae using only an autocatalytic reaction formula. We claimed that the system of the oscillating reaction involves an autocatalytic specie and more than one autocatalytic reaction in the CSTR. In addition, the autocatalytic reaction should be given by a positive feed-back system mathematically if we assume an output variable of the system to be an internal variable in differential equations that describe the system, and the equilibrium space for the variable should be constructed with a relation between the input and output of the system. Therefore, we have proposed that the oscillating reaction system involves multiple and complex positive feedback systems.

Appendix

If we assumed the system of reactions to be an ideal solution in pressure and thermal equilibrium, a mass reaction law could be introduced with a definition of the thermodynamic reaction rate (WATANABE, 1987). In recent years, some researchers have shown experimentally that this law does not satisfy a certain solution (HESHEL, 1993; SAGARA and YOSHIKAWA, 1997). However, we treat the system of reactions as an ideal solution and do not attempt to equate a system of reaction formulae in a non-equilibrium state.

We define a system of reaction formulae that describes each elementary reaction on the basis of HORIUCHI (1956). Both sides of the reaction formulae are multiplied by the continued ratio in which they react in the solution. We assume that all elementary reactions are caused by chance, with the same probability, and all densities of chemical species change at the same time in this system of reactions. Therefore, the rate equation for an arbitrary concentration variable of a chemical species is obtained by the sum of all first differentials for the concentration variable in each elementary reaction in which the chemical species takes part. Thus, we can transform a system of reaction formulae to a system of rate equations (HIROTA and KUWATA, 1972). We assume the whole of the reaction formulae to be $v_1, v_2, \ldots, v_N$, and a vector of reaction formulae to be $\mathbf{v} \equiv (v_1 \ldots v_N) \equiv \{N\text{-dimensional vector space spanned by reaction formulae } v_1, \ldots, v_N\}$. We also assume absolute values of stoichiometric coefficients for chemical species X_j ($j = 1, \ldots, n$) in the chemical equation for reaction formula v_k ($k = 1, \ldots, N$) to be m_{kj}, rate constants of forward and reverse reaction v_k to be α_k, β_k, sets of indices of all chemical species in each side, where there is the chemical specie X_j in the reaction formula v_k, to be $v_k(j)$, and sets of indices of all chemical species in those opposite sides to be $\overline{v_k(j)}$. A vector $\mathbf{x} \equiv {}^t(x_1, \ldots, x_n)$ is composed of concentration variables for all chemical species in the system of reaction formulae. If we describe the incremental rate for x_j in v_k as

$$g_j(v_k) = m_{kj}\left(-\alpha_k \prod_{l \in v_k(j)} x_l^{m_{kl}} + \beta_k \prod_{l \in \overline{v_k(j)}} x_l^{m_{kl}}\right), \tag{A.1}$$

then, with the addition of k as time as the number of reaction formulae, we could express a system of rate equations for the concentration variable x_j ($j = 1, \ldots, n$) of the chemical specie X_j in the system of reaction formulae as the following formula with tensor product:

$$\frac{d}{dt}\mathbf{x} = \left(\begin{pmatrix} g_1 \circ \\ \vdots \\ g_n \circ \end{pmatrix} \otimes \mathbf{v}\right) \mathbf{1}(\mathbf{N};\mathbf{n}) \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix} = \begin{pmatrix} g_1(v_1) & \cdots & g_1(v_N) \\ \vdots & \ddots & \vdots \\ g_n(v_1) & \cdots & g_n(v_N) \end{pmatrix} \mathbf{1}(\mathbf{N};\mathbf{n}) \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix}, \tag{A.2}$$

where $\mathbf{1}(\mathbf{N};\mathbf{n})$ is $\mathbf{N} \times \mathbf{n}$ matrix of which all elements are 1. Experimenters may say that this system of rate equations looks apart from real chemical systems because individual elementary reactions are interpreted by 1st order differential equations in most of the chemical reactions, where those inhomogeneous terms are linear or quadratic at most. However, there is a good possibility that a chemical specie participates in plural chemical reactions, simultaneously. Thus, we should study every possibility for reaction systems as complex systems, exhaustively. Based on this system of rate equations, we discussed the number of autocatalytic reactions in systems of the oscillating reaction in this paper.

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