Review

The general theory of stoichiometric number by Juro Horiuti—Application to the analysis of the stoichiometries of chemical oscillation systems

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Abstract

The stoichiometric relations of complex reaction networks were discussed with the general theory of stoichiometric number introduced and developed by Horiuti et al. Horiuti introduced the concept of reaction route in the theory, in which the reaction route was expressed by a set of stoichiometric numbers. The theory was applied to analyses of the stoichiometries in the reaction network of the 11 pseudo-elementary reactions (steps) of the Belousov–Zhabotinski (BZ) reaction and its reduced mechanism called the amplified Oregonator. Both of the mechanisms were developed by Noyes et al. for analysis of the oscillatory phenomena of the BZ reaction. The amplified Oregonator was concluded sufficiently to describe the stoichiometries of the original network of 11 steps by using the general theory of stoichiometric number. In comparison of these analyses of the stoichiometries in the above two mechanisms, a criterion for preserving overall stoichiometry in reduced mechanisms was introduced.
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1. Introduction

The concept of the stoichiometric number, introduced by Horiuti and Ikushima [1], has been developed by him and his coworkers [2–6]. The stoichiometric number theory has been developed to determine the stoichiometric number of the rate-determining step, thus contributing to the elucidation of the reaction mechanism [6–11]. Further, the general theory of stoichiometric number was found to provide a method for classification of complex reactions of so-called multiple reaction routes [4,5]. In this paper we deals with the latter case, i.e. the general theory of stoichiometric number.

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Stoichiometric relations among chemical species involved in a reaction, especially in a complex reaction, are of importance in description of the steady states and reaction mechanism. Horiuti and Nakamura developed the general theory of stoichiometric number, in which the concept of reaction route was introduced. Each of reaction routes is specified by a set of stoichiometric numbers. They showed that the reactions, consisting of elementary reactions (or steps), are classified by the number of reaction route. This theory had not been applied until the present author applied to analyses of complex reaction networks of chemical oscillation systems [12–14].

Reaction networks of most chemical oscillation systems are complicated and consist of many steps. Noyes and his coworkers precisely investigated the mechanism of the Belousov–Zhabotinski (BZ)

reaction. They interpreted oscillatory phenomena of the BZ reaction by the mechanism with ten steps [15], and then obtained the numerical solutions of limit cycle oscillation, using a model, called the Oregonator, which consists of five steps and three intermediates [16]. In improvement of their mechanism (for example, [17]), they proposed the reaction network of 11 pseudo-elementary reactions (steps) and its reduced mechanism called as the amplified Oregonator model of seven steps and five intermediates, and also obtained the numerical solutions of sustained oscillation [18,19]. When the reaction network of 11 steps was reduced to the amplified Oregonator of seven steps, they carefully discussed the stoichiometric relations of the two mechanisms. Noyes previously discussed how to reduce a complex network to the simpler one [20], adopting the multiplicity proposed by Corio [21].

In a reduced mechanism of a complex reaction network, stoichiometric relations of the reduced mechanism should be consistent with those of the complex reaction network at least at steady states. Applying the general theory of stoichiometric number introduced and developed by the late Prof. Horiuti, we already discussed [12] the stoichiometries of the Brusselator proposed by Prigogine and Lefever [22] for chemical oscillation phenomena and the Oregonator proposed by Field and Noyes [16]. Then we precisely discussed [13] the stoichiometric relations of the reaction networks of the BZ reaction, i.e. the reaction network of 11 steps and its reduced mechanism, the amplified Oregonator, proposed by Noyes and his coworkers [17–19]. In this discussion, we introduced a criterion for preserving overall stoichiometry in reduced mechanisms.

In the present memorial issue to the late Prof. Horiuti, we again carried out reconsideration of the stoichometric relations of the BZ reaction networks proposed by Noyes et al., which leads to further improvement and development with respect to reference [13]. First, we briefly describe the general theory of stoichiometric number and then discuss the stoichiometric relations of the reaction network of 11 steps and its reduced mechanism, the amplified Oregonator. On the basis of these discussion, we introduce a criterion for preserving overall stoichiometry in reduced mechanisms with an additional method. Finally, we discuss the reaction route in reaction networks of chemical oscillation systems.

1.1. The general theory of stoichiometric number and the reaction route

First, we describe the general theory of stoichiometric number including the concept of reaction route, by using the Brusselator [22], one of the simplest chemical oscillator, which is expressed by the following scheme:

$$A \rightarrow X \tag{1a}$$

$$B + X \rightarrow Y + D \tag{1b}$$

$$2X + Y \rightarrow 3X \tag{1c}$$

$$X \rightarrow E \tag{1d}$$

where A and B are reactants, D and E are products, and X and Y are intermediates.

In general, we consider a reaction network, which consists of S steps with I' intermediate species. In schemes (1a)–(1d), $S = 4$, and $I' = 2$. Net rate, v_s ($s = 1, 2, \ldots, S$) of each step is expressed by the forward rate, v_{+s}, and the reverse rate, v_{-s}, as

$$v_s = v_{+s} - v_{-s} \tag{2}$$

where v_s's are taken to be all positive at a steady state.

Denoting the amounts of species X and Y involved in the system of schemes (1a)–(1d) by X and Y, respectively, the kinetic equations are expressed by the net rates of respective steps, v_s's ($s = 1$–4 corresponding to steps (1a)–(1d)), as

$$\frac{\mathrm{d}X}{\mathrm{d}t} = v_1 - v_2 + v_3 - v_4 \tag{3a}$$

$$\frac{\mathrm{d}Y}{\mathrm{d}t} = v_2 - v_3 \tag{3b}$$

At a steady state, where $\mathrm{d}X/\mathrm{d}t = \mathrm{d}Y/\mathrm{d}t = 0$, we have from Eqs. (3a) and (3b):

$$v_3 = v_2, \qquad v_4 = v_1 \tag{4}$$

Taking v_1 and v_2 arbitrarily to be equal to 1 and 0, or equal to 0 and 1, respectively, we find it to be a solution of Eqs. (3a) and (3b). Any solution of Eqs. (3a) and (3b) at $\mathrm{d}X/\mathrm{d}t = \mathrm{d}Y/\mathrm{d}t = 0$ is expressed by a linear combination of two linearly independent solutions, $\boldsymbol{a}$ and $\boldsymbol{b}$, in the form of vector, respectively

$$\boldsymbol{a} \equiv (v_1^a, v_2^a, v_3^a, v_4^a) = (1, 0, 0, 1) \tag{5a}$$

$$\boldsymbol{b} \equiv (\nu_1^b, \nu_2^b, \nu_3^b, \nu_4^b) = (0, 1, 1, 0) \tag{5b}$$

as

$$\boldsymbol{v}(v_1, v_2, v_3, v_4) = V^a \cdot \boldsymbol{a} + V^b \cdot \boldsymbol{b} \tag{6}$$

i.e.

$$v_s = V^a \nu_s^a + V^b \nu_s^b, \quad s = 1, \ldots, 4 \tag{7}$$

Eq. (7) implies that the net rates, v_s's, of each steps of schemes (1a)–(1d) are expressed by two values, ν_s^a and ν_s^b of the independent solutions, $\boldsymbol{a}$ and $\boldsymbol{b}$, and two parameters, V^a and V^b. Each of the solutions, $\boldsymbol{a}$ and $\boldsymbol{b}$, is called a reaction route (simply route) and ν_s^a or ν_s^b is called the stoichiometric number of step s in route $\boldsymbol{a}$ or $\boldsymbol{b}$, respectively. In Eqs. (6) and (7), we can choose the coefficients, V^a and V^b, for real values of v_s's at a steady state. The coefficient V^a or V^b is called the rate of route $\boldsymbol{a}$ or $\boldsymbol{b}$, respectively.
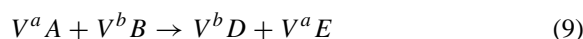
The stoichiometric expression for route $\boldsymbol{a}$ or $\boldsymbol{b}$ at a steady state is obtained as follows. Stoichiometric equations of steps (1a)–(1d), multiplied by the respective stoichiometric number ν_s^a or ν_s^b ($s = 1$–4), are added, to result in

$$\boldsymbol{a} : A \to E \tag{8a}$$

or

$$\boldsymbol{b} : B \to D \tag{8b}$$

respectively. Thus the stoichiometric expression, corresponding to the general solution (6), is given as

$$V^a A + V^b B \to V^b D + V^a E \tag{9}$$

In general, the amount of each of intermediates included in the system by X_i ($i = 1, 2, \ldots, I'$) and its differential with time, dX_i/dt, is expressed as a linear function of v_s's. At a steady state, $dX_i/dt = 0$ ($i = 1, 2, \ldots, I'$), we have I' linear equations. The number of independent equations in I' is denoted by I, which is called the number of independent intermediate. In these equations, the number of independent solutions denoted by P, is expressed by S and I as

$$P = S - I \tag{10}$$

In schemes (1a)–(1d), $S = 4$ and $I = 2$, and thus $P = 2$. Each independent solution is expressed by vectors, $\boldsymbol{v}^p$ ($p = 1, 2, \ldots, P$) as

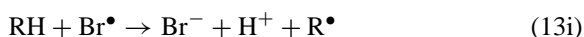$$\boldsymbol{v}^p = (\nu_1^p, \nu_2^p, \ldots, \nu_S^p) \tag{11}$$
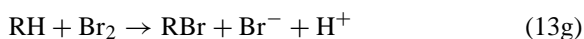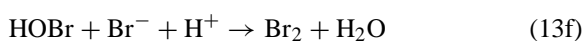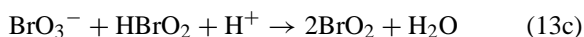
and the general solution is given by linear combination of the vectors, $\boldsymbol{v}^p$'s as

$$\begin{aligned} \boldsymbol{v} &= (v_1, v_2, \ldots, v_S) \\ &= \sum V^p \boldsymbol{v}^p \quad (p = 1, 2, \ldots, P) \end{aligned} \tag{12}$$

Practically we choose components of the independent solutions as simple numbers, e.g. positive integer or a half. Each of independent solutions, $\boldsymbol{v}^p$ ($p = 1, 2, \ldots, P$), is called *reaction route* $\boldsymbol{p}$ (simply route $\boldsymbol{p}$), each component, ν_s^p ($s = 1, 2, \ldots, S$), the stoichiometric number of step s in route $\boldsymbol{p}$, V^p ($p = 1, 2, \ldots, P$) the rate of route $\boldsymbol{p}$, I the number of independent intermediates, and P is the number of reaction route.

1.2. Application to the stoichiometry of the reaction network of 11 steps of the BZ reaction

We now apply our method to the reaction network of 11 steps for the BZ reaction proposed by Ruoff and Noyes [18], which is expressed as

$$BrO_3^- + Br^- + 2H^+ \to HBrO_2 + HOBr \tag{13a}$$

$$HBrO_2 + Br^- + H^+ \to 2HOBr \tag{13b}$$

$$BrO_3^- + HBrO_2 + H^+ \to 2BrO_2 + H_2O \tag{13c}$$

$$BrO_2 + M^{(n)+} + H^+ \to HBrO_2 + M^{(n+1)+} \tag{13d}$$

$$2HBrO_2 \to BrO_3^- + HOBr + H^+ \tag{13e}$$

$$HOBr + Br^- + H^+ \to Br_2 + H_2O \tag{13f}$$

$$RH + Br_2 \to RBr + Br^- + H^+ \tag{13g}$$

$$HOBr + R^\bullet \to ROH + Br^\bullet \tag{13h}$$

$$RH + Br^\bullet \to Br^- + H^+ + R^\bullet \tag{13i}$$

$$RH + M^{(n+1)+} \to M^{(n)+} + H^+ + R^\bullet \tag{13j}$$

$$2R^\bullet + H_2O \to RH + ROH \tag{13k}$$
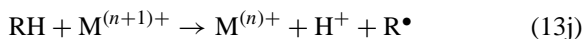
where RH is organic substrate, $R^\bullet$ its radical, and $M^{(n)+}$ and $M^{(n+1)+}$ are metal ion catalysts. In the reaction schemes (13a)–(13k), they claimed that there existed two different overall reactions, both of which, however, are described by the same stoichiometric expression, i.e.

$$BrO_3^- + 3RH + H^+ \to 2ROH + RBr + H_2O \tag{14}$$

First, we investigate the stoichiometry of the above reaction scheme by application of our method. In the above reaction scheme, there are nine intermediates, i.e. $HBrO_2$, $HOBr$, Br^-, $M^{(n+1)+}$, $M^{(n)+}$, BrO_2, Br_2, $Br^\bullet$, and $R^\bullet$, each of which is denoted by $X_1, X_2, \ldots, X_9$, respectively. Those amounts included in the system are expressed by italic $X_1, X_2, \ldots, X_9$. The net rates of (13a)–(13k) are denoted by $v_1, v_2, \ldots, v_{11}$, respectively. The kinetic equations with respect to the respective intermediates, $X_1, X_2, \ldots, X_9$, are expressed as

$$\frac{dX_1}{dt} = v_1 - v_2 - v_3 + v_4 - 2v_5 \tag{15a}$$

$$\frac{dX_2}{dt} = v_1 + 2v_2 + v_5 - v_6 - v_8 \tag{15b}$$

$$\frac{dX_3}{dt} = -v_1 - v_2 - v_6 + v_7 + v_9 \tag{15c}$$

$$\frac{dX_4}{dt} = v_4 - v_{10} \tag{15d}$$

$$\frac{dX_5}{dt} = -v_4 + v_{10} \tag{15e}$$

$$\frac{dX_6}{dt} = 2v_3 - v_4 \tag{15f}$$

$$\frac{dX_7}{dt} = v_6 - v_7 \tag{15g}$$

$$\frac{dX_8}{dt} = v_8 - v_9 \tag{15h}$$

$$\frac{dX_9}{dt} = -v_8 + v_9 + v_{10} - 2v_{11} \tag{15i}$$

At a steady state, $dX_i/dt = 0$ $(i = 1, 2, \ldots, 9)$, we obtain nine linear equations from Eqs. (15a)–(15i), but eight equations are independent each other since the equation obtain from Eq. (15d) is identical with that from Eq. (15e). The rank of matrix of the nine linear equations of 11 variables is easily found to be 8. Therefore, the number of independent intermediates I is 8 and the number of steps S is 11 so that the number of reaction route, P, is obtained from Eq. (10) as

$$P = S - I = 11 - 8 = 3$$

The number of reaction route $P = 3$ implies that there exist three independent solutions on kinetic Eqs. (15a)–(15i) under the steady state condition.

The eight variables of $v_4, \ldots, v_{11}$ are obtained as a solution from Eqs. (15a)–(15i) with $dX_i/dt = 0$ $(i = 1, 2, \ldots, 9)$ and are related each other in the following equations:

$$v_4 = 2v_3 \tag{16a}$$

$$v_5 = \tfrac{1}{2}(v_1 - v_2 + v_3) \tag{16b}$$

$$v_6 = \tfrac{1}{2}(v_1 + v_2 + v_3) \tag{16c}$$

$$v_7 = v_6 = \tfrac{1}{2}(v_1 + v_2 + v_3) \tag{16d}$$

$$v_8 = v_1 + v_2 \tag{16e}$$

$$v_9 = v_8 = v_1 + v_2 \tag{16f}$$

$$v_{10} = v_4 = 2v_3 \tag{16g}$$

$$v_{11} = v_3 \tag{16h}$$

where v_1, v_2, and v_3 are arbitrarily chosen. When three vectors of (v_1, v_2, v_3) are independent each other, we obtain three independent solutions of Eqs. (15a)–(15i) at a steady state. Let us choose (v_1, v_2, v_3) to be (2, 0, 0), (1, 1, 0), and (0, 0, 2), and the solutions, which are denoted by A, B, and C, respectively, can be obtained as

$$A = (2, 0, 0, 0, 1, 1, 1, 2, 2, 0, 0) \equiv (v_s^A),$$
$$s = 1\text{–}11 \tag{17a}$$

$$B = (1, 1, 0, 0, 0, 1, 1, 2, 2, 0, 0) \equiv (v_s^B),$$
$$s = 1\text{–}11 \tag{17b}$$

$$C = (0, 0, 2, 4, 1, 1, 1, 0, 0, 4, 2) \equiv (v_s^C),$$
$$s = 1\text{–}11 \tag{17c}$$

The general solution of Eqs. (15a)–(15i) at a steady state is expressed by a linear combination of A, B, and C as

$$v \equiv (v_1, v_2, v_3, v_4, v_5, v_6, v_7, v_8, v_9, v_{10}, v_{11})$$
$$= V^A \cdot A + V^B \cdot B + V^C \cdot C \tag{18}$$

Thus, the net rates v_s's of the respective steps are expressed as

$$v_s = V^A v_s^A + V^B v_s^B + V^C v_s^C, \quad s = 1\text{–}11 \tag{19}$$

Eq. (19) implies that the net rates v_s's at a steady state are described by three vectors A, B, and C, and

by three parameters, V^A, V^B, and V^C. Accordingly, the vector A, B, or C is called a reaction route (or simply route A, B, or C, respectively), the element of the vector, v_s^A, v_s^B, or v_s^C, is the stoichiometric number of step s in route A, B, or C, respectively, and the parameter V^A, V^B, or V^C, is the rate of route A, B, or C, respectively.

Stoichiometric expressions of routes A, B, and C are obtained as follows. Stoichiometric equations of steps s ($s = 1$–11), multiplied by the respective stoichiometric number, v_s^A, are added, to result in stoichiometric expression of route A, i.e.

$$BrO_3^- + 3RH + H^+ \rightarrow 2ROH + RBr + H_2O \quad (20)$$

The expressions of routes, B and C, similarly obtained, converged into Eq. (20). It may be noted that, if the respective steps of Eqs. (13a)–(13k) occur at v_s^A times ($s = 1$–11), route A of Eq. (20) is completed at a single occurrence. Similarly, the identical relationships are shown to be present in routes B and C.

Routes B and C, corresponding to the two overall reactions, were found by Ruoff and Noyes [18], but route A was not found by them. However, route A is necessary for description of the stoichiometry of the reaction, which consists of steps (13a)–(13k), at the steady state. These results show that the general theory of stoichiometric number can provide us the whole reaction routes in a complex reaction scheme without any omission.
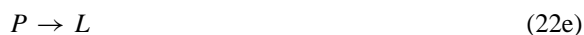
1.3. Stoichiometry of the amplified Oregonator

The reaction schemes (13a)–(13k) is too complicated to lead to numerical analysis of oscillatory phenomena. Field and Noyes proposed a simplified model, called the Oregonator [16], which consists of five steps including three intermediates, to the schemes (13a)–(13k). They succeeded to obtain the numerical solution of limit cycle oscillation, which was the first interpretation on BZ reaction. The Oregonator is shown as

$$A + Y \rightarrow X \quad (21a)$$

$$X + Y \rightarrow P \quad (21b)$$

$$B + X \rightarrow 2X + Z \quad (21c)$$

$$2X \rightarrow Q \quad (21d)$$

$$Z \rightarrow fY \quad (21e)$$

where X, Y, and Z are intermediates, A and B the reactants, P and Q the products, and f is a coefficient. Intermediates, X, Y, and Z, correspond to $HBrO_2$, Br^-, and Ce^{4+} ($M^{(n+1)+}$), respectively, included in schemes (13a)–(13k), respectively. In this case, $S = 5$ and $I = 3$, we see the number of reaction route, $P = 2$, from Eq. (10).

Ruoff and Noyes developed the Oregonator to the amplified Oregonator [18], which is shown as

$$A + Y \rightarrow X + P \quad (22a)$$

$$X + Y \rightarrow 2P \quad (22b)$$

$$A + X + C \rightarrow 2X + Z \quad (22c)$$

$$2X \rightarrow A + P \quad (22d)$$

$$P \rightarrow L \quad (22e)$$

$$P \rightarrow Y \quad (22f)$$

$$Z \rightarrow C \quad (22g)$$

where A is a reactant BrO_3^-, L a product RBr, and X, Y, Z, P, and C the intermediates, which correspond to $HBrO_2$, Br^-, and $2M^{(n+1)+}$, HOBr, and $2M^{n+}$, respectively. Relations of schemes (22a)–(22g) to schemes (13a)–(13k) are as follows. Steps (22a), (22b), and (22d) correspond to (13a), (13b), and (13e), respectively. Steps (22c), (22e), (22f), and (22g) were obtained from combinations of two steps: (13c) and (13d), (13f) and (13g), (13h) and (13i), and (13j) and (13k), respectively. In the above scheme, reactants and products, such as RH, H^+, ROH and H_2O were abbreviated and also intermediates, BrO_2, Br_2, $Br^\bullet$, and $R^\bullet$ in schemes (13a)–(13k) disappeared in simplification by combination of steps described already. It is noted that, at combination of steps (13c) and (13d), the expression of step (13d) is multiplied by a factor 2.

We now investigate the reduced schemes (22a)–(22g), by using the general theory of stoichiometric number. Amounts of intermediates X, Y, Z, C, and P are denoted by Y_1, Y_2, ..., Y_5, respectively, and the net rates of steps (22a)–(22g) are denoted by v_s' ($s = 1, 2, ..., 7$), respectively. Kinetic equations with respect to the respective intermediates are expressed as

$$\frac{dY}{dt} = Mv' \quad (23)$$

where

$$\mathbf{Y} = (Y_1, Y_2, Y_3, Y_4, Y_5) \tag{24a}$$

$$\mathbf{v}' = (v'_1, v'_2, v'_3, v'_4, v'_5, v'_6, v'_7) \tag{24b}$$

and

$$\mathbf{M} = \begin{pmatrix} 1 & -1 & 1 & -2 & 0 & 0 & 0 \\ -1 & -1 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 & 0 & 0 & 1 \\ 1 & 2 & 0 & 1 & -1 & -1 & 0 \end{pmatrix} \tag{24c}$$

The rank of matrix $\mathbf{M}$ is easily found to be 4 and the number of steps is 7, so that the number of reaction route P equals 3. At a steady state, $d\mathbf{Y}/dt = 0$, the net rates, v'_4, v'_5, v'_6, and v'_7, are expressed from Eq. (23) as

$$v'_4 = \tfrac{1}{2}(v'_1 - v'_2 + v'_3) \tag{25a}$$

$$v'_5 = \tfrac{1}{2}(v'_1 + v'_2 + v'_3) \tag{25b}$$

$$v'_6 = v'_1 + v'_2 \tag{25c}$$

$$v'_7 = v'_3 \tag{25d}$$

Taking (v'_1, v'_2, v'_3) to be $(2, 0, 0)$, $(1, 1, 0)$, and $(0, 0, 2)$, we obtain three independent routes, $\mathbf{A}'$, $\mathbf{B}'$, and $\mathbf{C}'$, respectively, from Eqs. (25a)–(25d), i.e.

$$\mathbf{A}' = (2, 0, 0, 1, 1, 2, 0) \equiv (v_s^{A'}), \quad s = 1\text{–}7 \tag{26a}$$

$$\mathbf{B}' = (1, 1, 0, 0, 1, 2, 0) \equiv (v_s^{B'}), \quad s = 1\text{–}7 \tag{26b}$$

$$\mathbf{C}' = (1, 0, 2, 1, 1, 0, 2) \equiv (v_s^{C'}), \quad s = 1\text{–}7 \tag{26c}$$

The general solution of Eq. (23) under the steady state condition, $d\mathbf{Y}/dt = 0$, is expressed as

$$\mathbf{v}' = V^{A'} \cdot \mathbf{A}' + V^{B'} \cdot \mathbf{B}' + V^{C'} \cdot \mathbf{C}' \tag{27}$$

Thus, the net rates, v_s's, of the respective steps are expressed as

$$v'_s = V^{A'} v_s^{A'} + V^{B'} v_s^{B'} + V^{C'} v_s^{C'}, \quad s = 1\text{–}7 \tag{28}$$

Stoichiometric expressions of routes $\mathbf{A}'$, $\mathbf{B}'$, and $\mathbf{C}'$ are the same and given by

$$A \rightarrow L \tag{29}$$

where A is BrO_3^- and L is RBr.

When reactants and products abbreviated in schemes (22a)–(22g) are one more expressed, the above expression becomes identical with Eq. (20). The net rates v_1, v_2, and v_5 of steps (13a), (13b), and (13e) should be equal to v'_1, v'_2, and v'_4 of steps (22a), (22b), and (22d), respectively, since the former three steps are identical to the latter three steps, respectively. Comparing Eq. (19) with Eq. (28), we obtain

$$V^A = V^{A'}, \qquad V^B = V^{B'}, \qquad V^C = V^{C'}$$

Thus, routes $\mathbf{A}'$, $\mathbf{B}'$, and $\mathbf{C}'$ are found to correspond to routes $\mathbf{A}$, $\mathbf{B}$, and $\mathbf{C}$ in schemes (13a)–(13k), respectively.

1.4. A criterion for preserving overall stoichiometry in reduced mechanisms

We have so far investigated the stoichiometries of reaction schemes (13a)–(13k) and its reduced schemes (22a)–(22g). We will now introduce "a criterion for preserving overall stoichiometry in reduced mechanisms" by investigation of the stoichiometric relations between them.

In reaction schemes (13a)–(13k), the stoichiometry at any steady state is described in Eq. (18), which is expressed by three reaction routes $\mathbf{A}$, $\mathbf{B}$, and $\mathbf{C}$, and three parameters (the rates of routes) V^A, V^B, and V^C. These parameters are dependent on experimental conditions since net rates, v_s's, of steps s ($s = 1\text{–}11$), depend on experimental conditions. Accordingly, each of the net rates, v_s's, is described in Eq. (19) and assumes to be a function of V^A, V^B and V^C. Eq. (18) is expressed by Eqs. (17a)–(17c) as
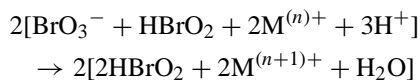
$$\begin{aligned} \mathbf{v} &= (v_1, v_2, v_3, v_4, v_5, v_6, v_7, v_8, v_9, v_{10}, v_{11}) \\ &= (2V^A + V^B, V^B, 2V^C, 4V^C, V^A + V^C, V^A \\ &\quad + V^B + V^C, V^A + V^B + V^C, 2V^A \\ &\quad + 2V^B, 2V^A + 2V^B, 4V^C, 2V^C) \end{aligned} \tag{30}$$

In the reduced schemes (22a)–(22g), Eq. (27) is expressed as

$$\begin{aligned} \mathbf{v}' &= (v'_1, v'_2, v'_3, v'_4, v'_5, v'_6, v'_7) \\ &= (2V^{A'} + V^{B'}, V^{B'}, 2V^{C'}, V^{A'}, V^{C'} + V^{A'}, V^{B'} \\ &\quad + V^{C'}, 2V^{A'} + 2V^{B'}, 2V^{C'}) \end{aligned} \tag{31}$$

First, we consider the case where we combine steps (13c) and (13d) to step (22c). Stoichiometric equations

of steps (13c) and (13d) are multiplied by $v_3^C (= 2)$ and $v_4^C (= 4)$, respectively, and are added to result in

$$2[\mathrm{BrO_3^-} + \mathrm{HBrO_2} + 2\mathrm{M}^{(n)+} + 3\mathrm{H}^+]$$
$$\rightarrow 2[2\mathrm{HBrO_2} + 2\mathrm{M}^{(n+1)+} + \mathrm{H_2O}]$$

which corresponds to step (22c), multiplied by a factor 2 and added by $3\mathrm{H}^+$ and $\mathrm{H_2O}$ which are abbreviated in the reduced schemes (22a)–(22g). A factor 2 corresponds to the stoichiometric number of $v_3^{C'}$. Therefore, the stoichiometry of the occurrence of $v_3^C (= 2)$ times of step (13c) and of $v_4^C (= 4)$ times of step (13d) is identical with that of the occurrence of $v_3^{C'} (= 2)$ times of step (22c). Thus, the occurrence of V^C times of route C, which implies the occurrence of $v_3^{C'} V^{C'}$ times of step (13c) and of $v_4^C V^C$ times of step (13d), corresponds to that of $V^{C'}$ times of route C', which implies the occurrence of $v_3^{C'} V^{C'}$ times of step (22c). This fact is shown in Eqs. (30) and (31).

Next, we consider the case of steps (13f) and (13g). In route A, stoichiometric equations of steps (13f) and (13g), multiplied by $v_6^A (= 1)$ and $v_7^A (= 1)$, respectively, are added to result in

$$\mathrm{HOBr} + 3\mathrm{RH} \rightarrow \mathrm{RBr} + \mathrm{H_2O} \tag{32}$$
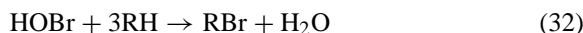
which corresponds to step (22e), in which 3RH and $\mathrm{H_2O}$ are abbreviated. In routes B and C, the same expression can be obtained. Therefore, the occurrence of $(V^A + V^B + V^C)$ times of the respective steps (13f) and (13g), corresponds to that of $(V^{A'} + V^{B'} + V^{C'})$ times of step (22e).

Similarly to the above described cases, the occurrence of $(2V^A + 2V^B)$ times of the respective steps of (13h) and (13I) is found to correspond to that of $(2V^{A'} + 2V^{B'})$ times of step (22f). Similarly, the occurrence of $4V^C$ times of step (13j), and $2V^C$ times of step (13k) corresponds to that of $2V^{C'}$ times of step (22g).

As discussed above, the stoichiometry of the reduced schemes (22a)–(22g) is consistent with that of the reaction schemes (13a)–(13k). Although the net rates, v_s's, of steps (13a)–(13k) vary with experimental conditions, expression (18) holds at another steady state at different V^A, V^B, and V^C, in which v_s's are expressed in Eqs. (19) and (30). When steps j and k are included in only one route (i.e. the stoichiometric numbers of steps j and k are zero except for only one route), it

is easily found that the stoichiometry of the resultant step gives that of steps j and k, as shown in the cases of the combination of steps (13c) and (13d) and of the combination of steps (13j) and (13k). When the stoichiometric numbers of steps j and k are not zero in two routes and those of steps j and k in one route are identical with those in another route, respectively, the resultant step gives the stoichiometry of steps j and k. This is shown in the case of steps (13h) and (13i), because the combination of two steps in two routes gives the same stoichiometric expression. The same holds in the case where the stoichiometric numbers of steps j and k are not zero in three routes as in the case of steps (13f) and (13g). However, if steps (13a) and (13b) are combined, the resultant step in route B' is expressed as

$$\mathrm{BrO_3^-} + 2\mathrm{Br} + 3\mathrm{H}^+ \rightarrow 3\mathrm{HOBr} \tag{33}$$
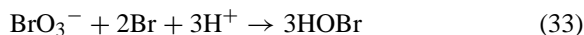
but the step in route A' remains in the same expression with (13a) multiplied by a factor 2. This discrepancy between the stoichiometric expressions of routes A' and B' implies that the combination of steps (13a) and (13b) does not hold for description of the stoichiometry of the reaction schemes (13a)–(13k).

We now extend the above discussion to general expression. In determination of the three routes A, B, and C, we choose simpler solutions, which can express the overall reaction (14). Since any linear combination of solutions A, B, and C, is a solution of Eqs. (15a)–(15i), we can choose another set of three independent solutions, each of which is given by a linear combination of A, B, and C, so that the conditions discussed above are not the ones necessary for the consistency of stoichiometry. When combining steps j and k in reaction schemes (13a)–(13k), we can obtain the relation between v_j and v_k in Eq. (30). Ratios of v_j/v_k of combined steps are given as

$$\frac{v_3}{v_4} = \frac{2V^C}{4V^C} = \frac{1}{2} \tag{34a}$$

$$\frac{v_6}{v_7} = \frac{V^A + V^B + V^C}{V^A + V^B + V^C} = 1 \tag{34b}$$

$$\frac{v_8}{v_9} = \frac{2(V^A + V^B)}{2(V^A + V^B)} = 1 \tag{34c}$$

$$\frac{v_{10}}{v_{11}} = \frac{4V^C}{2V^C} = 2 \tag{34d}$$

These ratios are independent of V^A, V^B, and V^C. At combination of steps (13a) and (13b), the ratio is expressed as

$$\frac{v_1}{v_2} = \frac{2V^A + V^B}{V^B} \tag{34e}$$

being dependent on V^A and V^B. The above relations do not depend on choice of the three independent routes, as shown in Appendix A.

Since the net rates v_s's vary with experimental conditions, the rates of routes V^A, V^B, and V^C vary with the conditions. When steps j and k are combined under the condition of a constant value of v_j/v_k as in the cases of Eqs. (34a)–(34d), the resultant step may give the stoichiomtry of steps j and k. On the other hand, if v_j/v_k depends on V^A, V^B, and/or V^C, v_j/v_k varied with experimental conditions so that the resultant step cannot give the stoichiometry of steps j and k. Therefore, we came to the result that the reduced scheme such as the amplified Oregonator has a criterion that the rate ratio, v_j/v_k, should not vary with the rate of reaction route in order to describe the same overall stoichiometry as in the full unreduced scheme.

The above criterion leads to another expression mathematically equivalent, which is shown by three Eqs. (A.5a)–(A.5c) in Appendix A, i.e.

$$v_j^A = r v_k^A \tag{35a}$$

$$v_j^B = r v_k^B \tag{35b}$$

$$v_j^C = r v_k^C \tag{35c}$$

where a constant r is the rate ratio v_j/v_k which is independent of V^A, V^B, and V^C. In the cases of Eqs. (34a)–(34d), Eqs. (35a)–(35d) are easily found to be fulfilled and in the case of Eq. (34e) not to be fulfilled. This expression is more convenient than the former for finding the consistency of the stoichiometric relation, which is found from Eqs. (17a)–(17c) of the independent reaction routes.

1.5. The reaction routes of chemical oscillation systems

In reaction schemes of chemical oscillation systems, there exists, at least, an unstable steady state, which may lead to limit cycle oscillation. Most chemical oscillation systems include so-called an autocatalytic process, such as steps (1c), (21c), and (22c),

which multiplies an intermediate 1.5 times in step (1c) and twice in steps (21c) and (22c). Although in reaction schemes (13a)–(13k) we cannot apparently find an autocatalytic process, the occurrence of both steps, (13c) and (13d), causes multiplication of an intermediate, $HBrO_2$, as already discussed. Even if we can obtain the numerical solutions of limit cycle oscillation from the unreduced schemes (13a)–(13k), we should appreciate the significance of the Oregonator and the amplified Oregonator since these reduced reaction schemes make it clear that the original reaction schemes (13a)–(13k) implicitly includes autocatalytic process.

Every reaction schemes of (1a)–(1d), (13a)–(13k), and (22a)–(22g), have multiple routes, as shown in Eqs. (5a), (5b) (17a)–(17c), and (26a)–(26c), respectively.[1] One of the respective routes in those three reaction schemes includes an autocatalytic process explicitly in both schemes (1a)–(1d) and (22a)–(22g), and implicitly in schemes (17a)–(17k). Each of these routes including an autocatalytic process may be unstable at each of respective steady states and the others may be stable. We may infer that the reaction schemes of chemical oscillation systems have both unstable and stable reaction routes. It is necessary to perform stability analysis in their routes.

2. Concluding remarks

In general, a reduced reaction scheme (mechanism) of a complex reaction network (scheme) includes several reduced steps, each of which is obtained from a combination of steps in the reaction network. As discussed above, the stoichiometry of the reaction network is described by reaction routes, each of which is expressed by the stoichiometric numbers of the constituent steps of the reaction network. The net rates v_s's of step s of the reaction network are expressed by the stoichiometric numbers of the steps in the respective reaction routes and their rates. At combination of two steps j and k of the reaction network, if a rate ratio of v_j/v_k expressed by the rates of the routes

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[1] Two reaction routes of reaction schemes (21a)–(21e) cannot be separated into a route including an autocatalytic step (21c) and that not including step (21c) since step (21e) was obtained by combination of too many steps to keep their stoichiometric validity. As a result of the combination a coefficient f was introduced.

and by the stoichiometric numbers is independent of the rate of the routes, the resultant step describes the stoichiometry of steps j and k. If not, the same does not hold. Stoichiometric equations of the two steps j and k, multiplied by the stoichiometric numbers of respective steps, are added and then the resultant step is obtained.

Therefore, in order that a reduced reaction scheme, obtained from a complex reaction network, describes the stoichiometry of the reaction network, it is necessary that rate ratios of v_j/v_k are independent of the rates of the reaction routes. Another expression of this statement is given by the relations of the stoichiometric numbers of steps j and k in the respective reaction routes, i.e. Eqs. (35a)–(35c). We call this fact as "a criterion for preserving overall stoichiometry in reduced mechanism".

The concept of the reaction route, which is shown to be useful for analyses of reaction networks, will be a powerful tool for stability analysis of a steady state of a complex reaction network. When each of reaction routes is separately analyzed with respect to its stability, we will well understand the mechanisms of chemical oscillation systems. This problem is left for the further studies in progress.

Acknowledgements

Appendix A

When net rates, v_j and v_k, of steps j and k are expressed as a function of V^A, V^B, and V^C of three independent routes, whether the rate ratio, v_j/v_k, gives a constant value or not is independent of choice of the three independent routes. This fact is verified as follows.

Let us express three independent routes as

$$\boldsymbol{A} = (v_1^A, \ldots, v_s^A, \ldots, v_S^A) \tag{A.1a}$$

$$\boldsymbol{B} = (v_1^B, \ldots, v_s^B, \ldots, v_S^B) \tag{A.1b}$$

$$\boldsymbol{C} = (v_1^C, \ldots, v_s^C, \ldots, v_S^C) \tag{A.1c}$$

and the general solution is expressed as

$$\boldsymbol{v} = (v_1, \ldots, v_s, \ldots, v_S)$$
$$= V^A \cdot \boldsymbol{A} + V^B \cdot \boldsymbol{B} + V^C \cdot \boldsymbol{C} \tag{A.2}$$

Consider a case where a rate ratio, v_j/v_k, is independent of V^A, V^B, and V^C, and we have

$$\frac{v_j}{v_k} = \frac{V^A v_j^A + V^B v_j^B + V^C v_j^C}{V^A v_k^A + V^B v_k^B + V^C v_k^C} = r \tag{A.3}$$

where r is a constant. We have from Eq. (A.3)

$$V^A(v_j^A - r v_k^A)$$
$$+ V^B(v_j^B - r v_k^B) + V^C(v_j^C - r v_k^C) = 0 \tag{A.4}$$

Since V^A, V^B, and V^C are variables, we have from Eq. (A.4)

$$v_j^A = r v_k^A \tag{A.5a}$$

$$v_j^B = r v_k^B \tag{A.5b}$$

$$v_j^C = r v_k^C \tag{A.5c}$$

Eqs. (A.5a)–(A.5c) are mathematically equivalent to Eq. (A.3).

Let us consider another set of three independent routes $\boldsymbol{A}'$, $\boldsymbol{B}'$, and $\boldsymbol{C}'$, which are given by linear combinations of $\boldsymbol{A}$, $\boldsymbol{B}$, and $\boldsymbol{C}$. We take $\boldsymbol{A}'$, $\boldsymbol{B}'$, and $\boldsymbol{C}'$ to be equal to $\boldsymbol{A}$, $\boldsymbol{B}$, and $(\beta \cdot \boldsymbol{B} + \gamma \cdot \boldsymbol{C})$, respectively, where β and γ are constant. If the rate ratio v_j/v_k expressed by routes, $\boldsymbol{A}'$, $\boldsymbol{B}'$, and $\boldsymbol{C}'$, gives the constant value of r, we will have the same relation in any set of three independent routes.

Stoichiometric numbers, $v_j^{C'}$ and $v_k^{C'}$, of route $\boldsymbol{C}'$ are expressed as

$$v_j^{C'} = \beta v_j^B + \gamma v_j^C \tag{A.6a}$$

$$v_k^{C'} = \beta v_k^B + \gamma v_k^C \tag{A.6b}$$

The net rates, v_j and v_k, are expressed, respectively, as

$$v_j = V^{A'} v_j^A + V^{B'} v_j^B + V^{C'} v_j^{C'} \tag{A.7a}$$

$$v_k = V^{A'} v_k^A + V^{B'} v_k^B + V^{C'} v_k^{C'} \tag{A.7b}$$

where $V^{A'}$, $V^{B'}$, and $V^{C'}$ are not identical with V^A, V^B, and V^C, respectively.

Substituting $\nu_j^{C'}$ and $\nu_k^{C'}$ from Eqs. (A.6a) and (A.6b) into Eqs. (A.7a) and (A.7b), respectively, we have

$$v_j = V^{A'} \nu_j^A + (V^{B'} + \beta V^{C'}) \nu_j^B + \gamma V^{C'} \nu_j^C \quad \text{(A.8a)}$$

$$v_k = V^{A'} \nu_k^A + (V^{B'} + \beta V^{C'}) \nu_k^B + \gamma V^{C'} \nu_k^C \quad \text{(A.8b)}$$

Substituting ν_j^A, ν_j^B and ν_j^C from Eqs. (A.5a)–(A.5c) into (A.8a), we have

$$v_j = r\{V^{A'} \nu_k^A + (V^{B'} + \beta V^{C'}) \nu_k^B + \gamma V^{C'} \nu_k^C\} \tag{A.9}$$

Thus, we have from (A.8b) and (A.9)

$$v_j = r v_k \tag{A.10}$$

which shows that the relation (A.3) is independent of choice of three independent routes. It may be noted that Eq. (A.3) is equivalent to Eqs. (A.5a)–(A.5c).

References

[1] J. Horiuti, M. Ikushima, Proc. Imp. Acad. Tokyo 15 (1939) 39.
[2] J. Horiuti, Chemical kinetics, Iwanami Series, Physics X.C. (1940) 2 (in Japanese).
[3] J. Horiuti, J. Res. Inst. Catal. Hokkaido Univ. 1 (1948) 8.
[4] J. Horiuti, T. Nakamura, Z. Phys. Chem. N. F. 11 (1957) 8.
[5] J. Horiuti, T. Nakamura, Advances in Catalysis, vol. 17, Academic Press, New York, 1967, p. 1.
[6] J. Horiuti, Ann. N. Y. Acad. Sci. 213 (1973) 5, and references therein.
[7] A. Kazusaka, J. Res. Inst. Catal. Hokkaido Univ. 19 (1971) 42.
[8] A. Kazusaka, I. Toyoshima, J. Res. Inst. Catal. Hokkaido Univ. 21 (1973) 150.
[9] K. Saito, M. Enyo, T. Matsushima, J. Res. Inst. Catal. Hokkaido Univ. 23 (1975) 26.
[10] M. Masuda, J. Res. Inst. Catal. Hokkaido Univ. 23 (1975) 122.
[11] M. Masuda, J. Res. Inst. Catal. Hokkaido Univ. 24 (1976) 83.
[12] M. Masuda, T. Nakamura, Chem. Eng. Commun. 82 (1989) 245.
[13] M. Masuda, J. Chem. Phys. 92 (1990) 6030.
[14] M. Masuda, J. Chem. Phys. 99 (1993) 4873.
[15] R.J. Field, E. Koros, R.M. Noyes, J. Am. Chem. Soc. 94 (1972) 8649.
[16] R.J. Field, M.R. Noyes, J. Chem. Phys. 60 (1974) 1877.
[17] R.M. Noyes, J. Chem. Phys. 80 (1984) 6071.
[18] P. Ruoff, R.M. Noyes, J. Chem. Phys. 84 (1986) 1413.
[19] P. Ruoff, R.M. Noyes, J. Chem. Phys. 89 (1988) 6247.
[20] R.M. Noyes, in: C. Vidal, A. Pacault (Eds.), Non-Equilibrium Dynamics in Chemical Systems, Springer, Berlin, 1984, pp. 60–64.
[21] P.L. Corio, J. Phys. Chem. 88 (1984) 1825.
[22] I. Prigogine, R. Lefever, J. Chem. Phys. 48 (1968) 1695.