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The Elimination of Fast Variables in Complex Chemical Reactions. I. Macroscopic Level

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The kinetics of complex chemical reactions is considered. Different time scales exist if one or more of the rate constants of the individual reaction steps is much larger than the others. Examples of specific reactions are given in which the intermediates vary on the fast time scale. They can be eliminated according to a standard scheme, the lowest order of which coincides with the steady-state approximation usually employed in textbooks on chemical kinetics.

KEY WORDS: Complex chemical reactions; elimination of fast variables; Brusselator.

1. INTRODUCTION

Consider the following chemical reaction:

$$A + B \rightarrow C \tag{1}$$

This equation states that one mole of substance A and one mole of substance B react together to form one mole of C. It represents the net effect of the reaction and is called the stoichiometric equation.

The reaction rate of (1) will depend on the concentrations of the reactants A and B and of the product C. If one denotes the concentrations by pairs of square brackets, the kinetic law can be written in the following way:

$$\frac{d}{dt}[C] = r\{[A], [B], [C]\} \tag{2}$$

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The function r is provided by experiment and depends on the mechanism of the reaction.

The mechanism of a reaction indicates how the reactants are transformed into products. The simplest possible mechanism for (1) is that the reaction proceeds by a single step: the formation of C is the result of a single collision between the molecules of the reactants A and B. Reactants of this kind are called simple.(1) They follow the law of mass action (Guldberg and Waage, 1867), which for the case of reaction (1) reads

$$\frac{d}{dt}[\mathrm{C}] = k[\mathrm{A}][\mathrm{B}] \tag{3}$$

The constant k is the familiar rate constant. The powers of the concentrations in the mass action expression are determined by the stoichiometry of the reaction, and therefore one says that the rate of a simple reaction follows the stoichiometry.

Reactions that proceed through a number of simple reaction steps are called complex.[3] Usually such a chain of reactions involves a number of intermediates, substances that are produced in an early stage of the reaction and consumed at a later stage, and therefore do not show up in the stoichiometric equation. It is surprising, however, that the concentrations of the intermediates do not appear in the overall reaction rate, although they determine the rates of the individual steps.

In order to derive the overall reaction rate of a complex chemical reaction one has to eliminate all intermediates.(6) The standard way to do this is based on the "steady-state hypothesis,"(1,2) which states that the concentrations of the intermediates are stationary.[4] This condition of stationarity implies that the concentrations of the intermediates can be expressed in terms of the concentrations of reactants and products. Consequently they can be eliminated from the overall reaction rate.

It has been noticed that the steady-state hypothesis is an approximation, which is valid if the concentrations of the intermediates are small compared to those of reactants and products, and which is only applicable after an initial "induction period" during which the intermediates approach their stationary values.(4) Although the steady-state hypothesis under these two limitations is basically correct, it has never been incorporated into a precise mathematical approximation scheme.

In this paper such a scheme will be provided. I will make use of the insight that the elimination of intermediates is nothing but an elimination

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[3] I am using the terminology of ref. 1, but other terminologies have been used (see ref. 2).

[4] This approach also goes under the name of the Bodenstein method.(6)

of fast variables.(4) The state of affairs may be described as follows. The reaction constants of the individual steps determine the time scales of the different stages of the overall reaction. If one of these reaction constants is much larger than the others, it may happen that the overall reaction consists of two stages that evolve on different time scales. A fast initial stage in which intermediates build up is followed by a slow second stage during which the formation of products is set and kept going. The first stage may be identified as the induction period, whereas the kinetics of the second stage is described by a reduced rate equation of the form (2).

Rate equations that contain two different time scales have been classified by Van Kampen.(4) Complex chemical reactions usually fall within the first category of this classification. The first category is characterized by the existence of a short initial period during which the fast variables adjust themselves to the conditions set by the slow variables. (In the terminology of Haken(9) the slow variables enslave the fast ones.)

In the first part of this paper, I investigate a standard textbook example of a complex chemical reaction: the formation of hydrogen bromide. A scaling of the intermediate variables is required in order to cast the rate equations into the standard form. They are of first category, and it turns out that the kinetics is characterized by three different time scales.

In the second part the importance of higher order calculations is demonstrated. It may happen that different plausible reaction mechanisms give different results for the overall reaction rate only in higher orders.

Finally, in the third part an extended version of the Brusselator(10) is studied. For this case the intermediates perform sustained oscillations. Fast oscillatory behavior belongs to the third categorie in Van Kampen's classification. Hence, a different elimination procedure is needed.

2. THE FORMATION OF HYDROGEN BROMIDE

The best-known example of a complex chemical reaction is the formation of hydrogen bromide, which can be found in almost every textbook on chemical kinetics. The stoichiometric equation reads

$$\mathrm{H_2 + Br_2 \rightarrow 2HBr} \tag{4}$$

The kinetic behavior was already studied in 1906.(5) It was found empirically that the reaction rate obeys the following law(1):

$$\frac{d}{dt}[\mathrm{HBr}] = \frac{k_t[\mathrm{H_2}][\mathrm{Br_2}]^{1/2}}{1 + k_i[\mathrm{HBr}][\mathrm{Br_2}]^{-1}} \tag{5}$$

In 1919 the following mechanism was proposed, which is considered to give an adequate description of this reaction. The constituting simple reaction steps, involving the intermediates H and Br, are given by

$$\mathrm{Br_2 + M \underset{2}{\overset{1}{\rightleftarrows}} 2Br + M} \tag{6}$$

$$\mathrm{Br + H_2 \underset{4}{\overset{3}{\rightleftarrows}} HBr + H} \tag{7}$$

$$\mathrm{H + Br_2 \xrightarrow{5} HBr + Br} \tag{8}$$

The letter M in (6) stands for any molecule; bromine may dissociate as a result of a collision with M.

If the concentrations are denoted by $[\mathrm{H_2}] = x_1$, $[\mathrm{Br_2}] = x_2$, $[\mathrm{HBr}] = x_3$, $[\mathrm{H}] = x_4$, $[\mathrm{Br}] = x_5$, and $[\mathrm{M}] = m$, the rate equations read

$$\frac{d}{dt} x_1 = k_3 x_1 x_5 - k_4 x_3 x_4 \tag{9}$$

$$\frac{d}{dt} x_2 = -k_1 m x_2 + k_2 m x_5^2 - k_5 x_2 x_4 \tag{10}$$

$$\frac{d}{dt} x_3 = k_3 x_1 x_5 - k_4 x_3 x_4 + k_5 x_2 x_4 \tag{11}$$

$$\frac{d}{dt} x_4 = k_3 x_1 x_5 - k_4 x_3 x_4 - k_5 x_2 x_4 \tag{12}$$

$$\frac{d}{dt} x_5 = 2k_1 m x_2 - 2k_2 m x_5^2 - k_3 x_1 x_5 + k_4 x_3 x_4 + k_5 x_2 x_4 \tag{13}$$

I have written down all five rate equations, but only three of them are independent, as there are two constants,

$$C_1 = 2x_1 + x_3 + x_4, \qquad C_2 = 2x_2 + x_3 + x_5 \tag{14}$$

Equations (11)–(13) are chosen as the independent ones. The variables x_1 and x_2 may be eliminated by using (14), but I will not do this explicitly.

Equations (11)–(13) contain all information about the various rate processes that play a role in the complex HBr reaction. As it is impossible to solve these equations exactly, we need an approximation method in order to get insight into the kinetics of the reaction.

An approximate solution may be obtained if one of the reaction constants k_i ($i = 1, \ldots, 5$) is much larger than the others. Then there will be fast and slow variables, and the fast ones may be eliminated. Which of the k_i will be the largest? The intermediates H and Br are much more reactive than H_2, Br_2 and HBr. Hence, qualitatively one may expect that a reaction step will proceed faster the more intermediates are among the output chemicals and the less intermediates (the more stable substances) are among the output chemicals. These considerations suggest that the second reaction is much faster than the others. So let us put

$$k_2/k_1 = 1/\varepsilon, \qquad \varepsilon \ll 1 \tag{15}$$

Apparently this assumption turns x_5 into a fast variable and x_3 and x_4 into slow variables [see (11)–(13)]. There is, however, a complication, which may be inferred from (13). If one considers this equation on the fast time scale ($\tau = t/\varepsilon$) and lets $\varepsilon \to 0$, then x_5 evolves according to

$$\frac{d}{d\tau} x_5 = -2k_1 m x_5^2 \tag{16}$$

Hence $x_5 \to 0$, but only very slowly (power law). In the standard scheme$^{(4)}$ it is assumed that the fast variables approach their quasistationary values exponentially fast. Hence, the standard scheme cannot be applied to Eq. (11)–(13) as they stand.

However, it is possible to transform (11)–(13) into the standard form. One must realize that (16) is only valid for $\varepsilon = 0$. For finite ε, (16) only applies as long as x_5 is of order one. If x_5 becomes of order $\sqrt{\varepsilon}$, it will no longer rapidly decrease, as the rate of change due to the first reaction will be of the same order as that due to the second. Similar considerations apply to the variable x_4 (it will rapidly decrease unless it is of order $\sqrt{\varepsilon}$). Hence as soon as x_4 and x_5 attain values of order $\sqrt{\varepsilon}$, a new kinetic regime is entered. In order to study this kinetic regime, we perform the following scaling:

$$x_4 = \varepsilon^{1/2} z_1, \qquad x_5 = \varepsilon^{1/2} z_2 \tag{17}$$

Incidentically, under experimental conditions in which initially only H_2 and Br_2 are present and H and Br are produced during the reaction, this regime will be automatically attained.

In terms of the new variables z_1 and z_2 the rate equations read

$$\frac{d}{dt} x_3 = \varepsilon^{1/2}(k_3 x_1 z_2 - k_4 x_3 z_1 + k_5 x_2 z_1) \tag{18}$$

$$\frac{d}{dt} z_1 = k_3 x_1 z_2 - k_4 x_3 z_1 - k_5 x_2 z_1 \tag{19}$$

$$\frac{d}{dt} z_2 = \frac{2mk_1}{\sqrt{\varepsilon}} (x_2 - z_2^2) - k_3 x_1 z_2 + k_4 x_3 z_1 + k_5 x_2 z_1 \tag{20}$$

Now the rate equations are in the standard form. Moreover, they clearly display the presence of three time scales in the HBr reaction. The variable x_3 varies much more slowly than z_1 and z_2, which will be eliminated sucessively in the next section.

3. SUCESSIVE ELIMINATION OF FAST VARIABLES

The standard scheme for elimination of fast variables(4) has been formulated for two time scales. The generalization to more time scales, however, is straightforward: one just reduces the number of time scales step by step.

First we will eliminate the variable that varies most rapidly. For that end the following perturbation series is introduced:

$$z_2 = z_2^{(0)} + \varepsilon^{1/2} z_2^{(1)} + \cdots \tag{21}$$

According to (14) and (17), this expansion induces two other perturbation series,

$$x_1 = x_1^{(0)} + \varepsilon^{1/2} x_1^{(1)} + \cdots, \qquad x_2 = x_2^{(0)} + \varepsilon^{1/2} x_2^{(1)} + \cdots \tag{22}$$

where

$$x_1^{(n)} = -\tfrac{1}{2} z_1^{(n-1)}, \qquad x_2^{(n)} = -\tfrac{1}{2} z_2^{(n-1)}, \qquad n = 1, 2,..$$

The different orders of (21) are determined by substituting (21) and (22) into (20) and solving the resulting equation order by order. In lowest order one finds

$$z_2^{(0)} = (x_2^{(0)})^{1/2} \tag{23}$$

The first order yields [note $(d/dt)\, z_2^{(0)} \sim \sqrt{\varepsilon}$]

$$4mk_1 (x_2^{(0)})^{1/2} z_2^{(1)} = 2mk_1 x_2^{(1)} - k_3 x_1^{(0)} (x_2^{(0)})^{1/2} + (k_4 x_3 + k_5 x_2^{(0)})\, z_1 \tag{24}$$

One obtains reduced rate equations by substituting (23) and (24) into (18) and (19)

$$\frac{d}{dt} x_3 = \varepsilon^{1/2} [k_3 x_1 (x_2^{(0)})^{1/2} - k_4 x_3 z_1 + k_5 x_2 z_1] + \varepsilon k_3 x_1 z_2^{(1)} + \cdots \tag{25}$$

$$\frac{d}{dt} z_1 = k_3 x_1 (x_2^{(0)})^{1/2} - (k_4 x_3 + k_5 x_2)\, z_1 + \varepsilon^{1/2} k_3 x_1 z_2^{(1)} + \cdots \tag{26}$$

One must bear in mind that x_1 and x_2 contain different orders according to (22). Only two time scales remain in (25) and (26), and as z_1 varies faster than x_3, the elimination procedure can now be repeated.

In order to eliminate z_1, put

$$z_1 = z_1^{(0)} + \varepsilon^{1/2} z_1^{(1)} + \cdots \tag{27}$$

Substitute (27) in (26) and apply (22). The zeroth-order terms yield

$$z_1^{(0)} = k_3 x_1^{(0)} (x_2^{(0)})^{1/2} \,(k_4 x_3 + k_5 x_2^{(0)}) \tag{28}$$

For the first order one has

$$(k_4 x_3 + k_5 x_2^{(0)})\, z_1^{(1)} = k_3 x_1^{(1)} (x_2^{(0)})^{1/2} + k_3 x_1^{(0)} z_2^{(1)} - \frac{1}{\sqrt{\varepsilon}} \frac{d}{dt} z_1^{(0)} . \tag{29}$$

If one uses the results (28) and (29) in (25), one obtains the rate equation that describes the slow production of HBr;

$$\begin{aligned} \frac{d}{dt} x_3 = {} & 2\varepsilon^{1/2} k_3 k_5 x_1^{(0)} x_2^{(0)} (x_2^{(0)})^{1/2} \,(k_4 x_3 + k_5 x_2^{(0)})^{-1} \\ & + \varepsilon k_3 x_1^{(0)} z_2^{(1)} + \varepsilon (k_5 x_2^{(0)} - k_4 x_3)\, z_1^{(1)} \\ & - \tfrac{1}{2} \varepsilon (k_3 + k_5)(x_2^{(0)})^{1/2} \, z_1^{(0)} - \tfrac{1}{4} \varepsilon k_3 x_1^{(0)} \end{aligned} \tag{30}$$

The lowest order coincides with the empirical law (5), and one obtains the familiar expressions(1)

$$k_t = 2k_3 (k_1/k_2)^{1/2}, \qquad k_i = k_4/k_5 \tag{31}$$

By a small calculation the first-order correction of (30) can be found explicitly. From (24) and (29) it follows that

$$z_2^{(1)} = -\tfrac{1}{4} \tag{32}$$

$$\begin{aligned} z_1^{(1)} = {} & -\tfrac{1}{4} k_3 x_1^{(0)} (k_4 x_3 + k_5 x_2^{(0)})^{-2} \,[k_4 x_3 + (k_5 + 2k_3)\, x_2^{(0)}] \\ & + \tfrac{1}{2} k_3^2 k_5 x_1^{(0)} x_2^{(0)} (k_4 x_3 + k_5 x_2^{(0)})^{-4} \\ & \times [2k_4 x_1^{(0)} x_3 + 2k_5 (x_2^{(0)})^2 + k_4 x_1^{(0)} x_3 + (4k_4 - k_5)\, x_1^{(0)} x_2^{(0)}] \end{aligned} \tag{33}$$

One can pursue the calculations to higher orders, but after the first order they become very cumbersome.

What about the validity of (30)? It is clear that (30) only applies if both fast variables have attained their quasistationary values (23) and (28). There is an initial period in time during which the concentrations of intermediates H and Br build up, and (30) does not apply. This is the induction period. Its structure follows from (20) and (26). There are two stages: first z_2 approaches the value (23) in a time of order $\sqrt{\varepsilon}$, and subsequently z_1

tends to the value (28) in a time of order one. As the time during which an appreciable amount of HBr is produced is of the order $1/\sqrt{\varepsilon}$, the induction period is relatively small.

4. THE REACTION BETWEEN NITRIC OXIDE AND HYDROGEN

In order to derive the overall rate of a complex chemical reaction one needs a reaction mechanism, which consists of a chain of simple reaction steps. It may happen that there exists more than one plausible reaction scheme that reproduces the correct overall reaction rate (in lower order). In this case higher order corrections become important, as they may help to distinguish among the different mechanisms.

In order to illustrate this point, we consider the following reaction:

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O \tag{34}$$

The reaction rate was found to be$^{(7)}$

$$\frac{d}{dt}[H_2O] = 2k[NO]^2[H_2] \tag{35}$$

There are two mechanisms, involving, respectively, the intermediates H_2O_2 and N_2O, through which the reaction may proceed.$^{(8)}$ Both mechanisms consist of two steps, the initiation of the intermediate followed by a rapid termination.

The first mechanism reads:

$$2NO + H_2 \xrightarrow{1} N_2 + H_2O_2 \tag{36}$$

$$H_2O_2 + H_2 \xrightarrow{2} 2H_2O \tag{37}$$

Denote the concentrations by $[NO] = x_1$, $[H_2] = x_2$, $[N_2] = x_3$, $[H_2O] = x_4$ and $[H_2O_2] = x_5$. Only two of these variables are independent, say x_4 and x_5. The others can be expressed in terms of them,

$$x_1 = C_1 - x_4 - 2x_5, \qquad x_2 = C_2 - x_4 - x_5, \qquad x_3 = C_3 + \tfrac{1}{2}x_4 + x_5 \tag{38}$$

The rate equations read

$$\frac{d}{dt}x_4 = 2k_2x_2x_5 \tag{39}$$

$$\frac{d}{dt}x_5 = k_1x_1^2x_2 - k_2x_2x_5 \tag{40}$$

It is understood that x_1 and x_2 are given by (38).

Assume now that the second step (37) proceeds much faster than the first; $k_2/k_1 = 1/\varepsilon$, $\varepsilon \ll 1$. It is possible to introduce the slow variable $x_4 + 2x_5$ and subsequently eliminate the fast variable x_5. I prefer, however, to perform the scaling $x_5 = \varepsilon z$, which also brings the rate equations into the standard form

$$\frac{d}{dt} x_4 = 2k_1 x_2 z \tag{41}$$

$$\frac{d}{dt} z = \frac{1}{\varepsilon} k_1 x_2 (x_1^2 - z) \tag{42}$$

The fast variable z is expanded as $z = z^{(0)} + \varepsilon z^{(1)} + \cdots$. According to (38), this induces the following series:

$$x_1 = x_1^{(0)} + \varepsilon x_1^{(1)} + \cdots \quad (x_1^{(n)} = -2z^{(n-1)}, \quad n \geqslant 1)$$
$$x_2 = x_2^{(0)} + \varepsilon x_2^{(1)} + \cdots \quad (x_2^{(n)} = -z^{(n+1)}, \quad n \geqslant 1)$$

The first three orders of (42) yield

$$z^{(0)} = (x_1^{(0)})^2, \qquad z^{(1)} = 0, \qquad z^{(2)} = (4x_1^{(0)})^4 \tag{43}$$

Hence, for the reduced rate equation one gets

$$\frac{d}{dt} x_4 = 2k_1 x_2^{(0)} (x_1^{(0)})^2 - 8\varepsilon^2 k_1 x_2^{(0)} (x_1^{(0)})^4 - 4\varepsilon^2 k_1 (x_1^{(0)})^6 + \cdots \tag{44}$$

In zeroth order one thus recovers the empirical law (35).

There is a second mechanism that reproduces (35). The reaction steps are

$$2NO + H_2 \xrightarrow{3} N_2O + H_2O \tag{45}$$

$$N_2O + H_2 \xrightarrow{4} N_2 + H_2O \tag{46}$$

The concentration of the intermediate N_2O is denoted by x_6, and the rate equations are

$$\frac{d}{dt} x_4 = k_3 x_1^2 x_2 + k_4 x_2 x_6 \tag{47}$$

$$\frac{d}{dt} x_6 = k_3 x_1^2 x_2 - k_4 x_2 x_6 \tag{48}$$

The dependent variables x_1 and x_2 obey

$$x_1 = D_1 - x_4 - x_6, \qquad x_2 = D_2 - x_4 \tag{49}$$

Assume that reaction (46) is much faster than (45); $k_4/k_3 = \delta$, $\delta \ll 1$. The scaling $x_6 = \delta z$ transforms the rate equation into

$$\frac{d}{dt} x_4 = k_3(x_1^2 x_2 + x_2 z) \tag{50}$$

$$\frac{d}{dt} z = \frac{1}{\delta} k_3 x_2 (x_1^2 - z) \tag{51}$$

Performing the standard computations, one obtains for the reduced rate equation

$$\frac{d}{dt} x_4 = 2k_3 (x_1^{(0)})^2 + 4\delta k_3 x_2 (x_1^{(0)})^3 + \cdots \tag{52}$$

Again the zeroth order coincides with (35).

As the correction terms in (44) and (52) differ, the question of which mechanism is actually realized can be answered by carefully measuring the deviations from (35).

5. THE EXTENDED BRUSSELATOR

Intermediates may perform sustained oscillations. This kind of behavior occurs if at the level of the rate equations a limit cycle exists. If the period of the limit cycle is much smaller than the time on which other chemical transformations take place, the intermediates are fast variables and may be eliminated. However, the elimination procedure is different from the one that was employed in the former examples. I will use an extended version of the well-known Brusselator(10) to illustrate the state of affairs.

The chain of reactions for the Brusselator is given by

$$\mathrm{A} \xrightarrow{1} \mathrm{X} \tag{53}$$

$$\mathrm{B} + \mathrm{X} \xrightarrow{2} \mathrm{Y} + \mathrm{D} \tag{54}$$

$$2\mathrm{X} + \mathrm{Y} \xrightarrow{3} 3\mathrm{X} \tag{55}$$

$$\mathrm{X} \xrightarrow{4} \mathrm{E} \tag{56}$$

The net effect of the Brusselator is that the input chemicals A and B are transformed into the products D and E. In the standard treatment of the

Brusselator one assumes that the concentrations of A and B are maintained constant. For a certain range of values of the rate constants it can then be shown that X and Y perform stable oscillations along a limit cycle.(11)

Here, however, we are interested in the situation that A and B are not held constant but are depleted according to (53) and (54). It will be assumed that the amount of A and B consumed during one period of oscillation is very small. The aim is to derive an equation that describes the slow decrease of A and B after many oscillations.

Let us denote the concentrations of the chemicals by $[A]=x_1$, $[B]=x_2$, $[X]=x_3$, and $[Y]=x_4$. The rate equations may then be written as

$$\frac{d}{dt}x_1 = -k_1 x_1 \tag{57}$$

$$\frac{d}{dt}x_2 = -k_2 x_2 x_3 \tag{58}$$

$$\frac{d}{dt}x_3 = k_1 x_1 - k_2 x_2 x_3 + k_3 x_3^2 x_4 - k_4 x_3 \tag{59}$$

$$\frac{d}{dt}x_4 = k_2 x_2 x_3 - k_3 x_3^2 x_4 \tag{60}$$

If one puts

$$k_1 = \varepsilon\alpha k_2, \qquad k_3 = (\beta/\varepsilon)^2 k_2, \qquad k_4 = \alpha k_2 \tag{61}$$

with $\varepsilon \ll 1$, and introduces the scaled variables z_1 and z_2 according to

$$x_3 = (\varepsilon/\beta)^{1/2} z_1, \qquad x_4 = (\varepsilon/\beta)^{1/2} z_2 \tag{62}$$

the rate equations transform into (furthermore absorb a factor k_2 in the time scale; see ref. 18)

$$\frac{d}{dt}x_1 = -\varepsilon\alpha x_1 \tag{63}$$

$$\frac{d}{dt}x_2 = -\varepsilon\beta^{-1} x_2 z_1 \tag{64}$$

$$\frac{d}{dt}x_1 = \alpha\beta x_1 - \alpha z_1 + z_1^2 z_2 - x_2 x_1 \tag{65}$$

$$\frac{d}{dt}x_2 = x_2 z_1 - z_1^2 z_2 \tag{66}$$

These are the rate equations of the extended Brusselator. They clearly exhibit that the input chemicals A and B are only slowly depleted. For $\varepsilon = 0$, x_1 and x_2 are constant and one recovers the ordinary Brusselator.

6. ELIMINATION OF FAST OSCILLATIONS

The rate equations (63)–(66) designate z_1, z_2 and x_1, x_2 as fast and slow variables, respectively. How does one eliminate the fast variables and derive reduced equations for the slow ones?

Let us first study (65) and (66) for constant x_1 and x_2 ($\varepsilon = 0$). There is one stationary point given by

$$z_1 = \beta x_1, \qquad z_2 = \beta^{-1} x_1^{-1} x_2 \tag{67}$$

A limit cycle exists if the stationary point is unstable. The condition of instability is given by $x_2 > \alpha + \beta^2 x_1^2$. In this regime any solution of (65) and (66) will first approach the limit cycle and subsequently perform sustained oscillations along the limit cycle. The motion perpendicular to the limit cycle is of the first category, whereas the oscillatory behavior falls within the third category.(4) This determines the elimination procedure.

Only the decay of x_2 is affected by the motion of z_1 and z_2. The lowest order effect of the limit-cycle oscillations can be found by an averaging procedure,(14,15)

$$\frac{d}{dt} x_2 = -\varepsilon \beta^{-1} x_2 \overline{z_1}(x_1, x_2) \tag{68}$$

$\overline{z_1}(x_1, x_2)$ is the time average along the limit cycle.

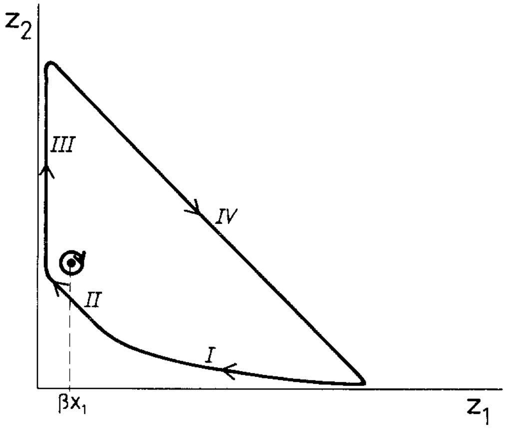

Fig. 1. Small and large limit cycle of the Brusselator.

The limit cycle of (65) and (66) encircles the unstable stationary point (67) (see Fig. 1). Hence, for very small limit cycles ($x_2 \geqslant \alpha + \beta^2 x_1^2$) one will have $\overline{z_1} = \beta x_1$, and the reduced equation (68) becomes

$$\frac{d}{dt} x_2 = -\varepsilon x_1 x_2 \tag{69}$$

Large limit cycles appear if $x_2 \gg \alpha + \beta^2 x_1^2$ (large instability of stationary point). It turns out that $\overline{z_1}$ can be determined in this limit.(18) For that end one has to calculate the limit cycle in full detail, which can be done by a standard procedure.

Surprisingly, the result coincides with the small-limit-cycle expression: $\overline{z_1} = \beta x_1$. Hence, (68) also applies for large limit cycles. This result, however, is merely a peculiarity of the Brusselator; one can show that it does not hold for other models.

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