

About Bifurcational Parametric Simplification

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Abstract. A concept of “critical” simplification was proposed by Yablonsky and Lazman (1996) for the oxidation of carbon monoxide over a platinum catalyst using a Langmuir-Hinshelwood mechanism. The main observation was a simplification of the mechanism at ignition and extinction points. The critical simplification is an example of a much more general phenomenon that we call a *bifurcational parametric simplification*. Ignition and extinction points are points of steady state multiplicity bifurcations, i.e., they are points of a corresponding bifurcation set for parameters.

Any bifurcation produces a dependence between system parameters. This is a mathematical explanation and/or justification of the “parametric simplification”. It leads us to a conjecture that “maximal bifurcational parametric simplification” corresponds to the “maximal bifurcation complexity.”

This conjecture can have practical applications for experimental study, because at points of “maximal bifurcation complexity” the number of independent system parameters is minimal and all other parameters can be evaluated analytically or numerically.

We illustrate this method by the case of the simplest possible bifurcation, that is a multiplicity bifurcation of steady state and we apply this analysis to the Langmuir mechanism. Our analytical study is based on a coordinate-free version of the method of invariant manifolds by Bykov, Goldfarb, Gol'dshtein (2006). As a result we obtain a more accurate description of the “critical (parametric) simplifications.”

With the help of the “bifurcational parametric simplification” kinetic mechanisms and reaction rate parameters may be readily identified from a monoparametric experiment (reaction rate vs. reaction parameter).

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1. Introduction and methodology

By a standard linguistic definition, a bifurcation is a place where something divides into two branches. Typical examples are: bifurcation of aorta is the region in which the abdominal aorta bifurcates into the left and right branches; river bifurcation, the forking of a river into its distributaries; bifurcation of

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trachea, etc... For all these examples, bifurcations are places where the main stream is divided into two or more streams. This dynamical interpretation corresponds to geometric changes of objects.

This simplistic meaning of bifurcation can be extended. Roughly speaking, a bifurcation is a region of qualitative changes in the system's dynamical behavior. It can be induced by changes in geometry, but also by other causes.

The notion of "bifurcation" in mathematics was introduced by Henri Poincaré [14] at the end of nineteenth century for changes in the multiplicity of steady states for systems of ordinary differential equations (ODE). Nowadays, this notion is used for systems of partial differential equations (PDE) and all other types of continuous and discrete mathematical models. Any mathematical model, except for a set of variables that describes its dynamical behavior, also has a set of parameters that are "permanent" comparatively with variables. In reality these parameters are control parameters and the system's asymptotic dynamics (for example, the steady states multiplicity) depends on its values.

Roughly speaking, a mathematical bifurcation is a qualitative change of asymptotic dynamics due to a smooth and slow change in the values of the parameters. A typical example is the famous Hopf bifurcation that describes a change from a steady state to oscillations. These qualitative changes can be continuous and slow (bifurcation theory) but can be also fast and even very fast (catastrophe theory).

Let us recall that "bifurcation theory studies and classifies phenomena characterized by sudden shifts in behavior arising from small changes in circumstances, analyzing how the qualitative nature of equation solutions depends on the parameters that appear in the equation" ([1]). Analysis of complex bifurcation points is a classical subject of the theory of dynamical system ([1]).

Mathematical Catastrophe theory was invented by Rene Thom in the book *Stabilite Structurelle et Morphogenese*, published in 1972 [15]. He proposed a classification of simple catastrophes using geometric properties of surfaces in multidimensional spaces. By E.C. Zeeman "the world is full of sudden transformations and unpredictable divergences" that are subjects in Catastrophe theory [21]. One of the possible explanations of such "sudden transformations" is the existence of fast sub-processes into an original system, that relax very quickly to its new asymptotic state. This fast relaxation is very hard to observe.

A set of parameters where a bifurcation or a catastrophe occurs is called a bifurcation set B . It is a subset of the space of parameters P and the dimension of the bifurcation set is less than the dimension of P . Typically it is a surface in P . The dimension of P ($\dim P$) is the number of independent parameters. Because $\dim B$ is less than $\dim P$, the number of independent parameters of B is less than $\dim P$, and a corresponding part of the parameters $m = \dim P - \dim B$ depends on others.

We call this phenomenon as "bifurcational parametric simplification".

The number m is called a bifurcational simplification number.

Conjecture 1.1. The maximal bifurcational simplification number corresponds to a bifurcation of "maximal complexity."

The conjecture is more philosophical than it looks. The maximal bifurcational simplification number is clear, but what is a bifurcation of maximal complexity? This question arises because there exist different types of bifurcations: change of stability, Hopf bifurcation, multiplicity of limit cycles, non local bifurcations etc... In our opinion, a more accurate understanding of the maximal bifurcation complexity depends on modeling phenomena.

The bifurcational parametric simplification was first described in papers of Yablonsky et al. [19], [20] under the name of "critical simplification" for the famous Langmuir absorption model of heterogeneous catalytic kinetics. They observed an essential simplification of the kinetics at extinction and ignition points that permitted them to find simple connections between the values of "bifurcation parameters" and kinetic constants [20], [13]. As a "bifurcation parameter" was used the maximal kinetic rate R_3 , is an observable quantity. At ignition and extinction points R_3 is equal to the kinetic constants of absorption and desorption, that in turn can be employed to applications involving kinetic constant measurements.

The Langmuir absorption model combine fast and slow kinetic processes. Ignition and extinction points are points of fast bifurcations (catastrophes).

1.1. Discussion about "maximal complexity"

We start from an historical remark. In 1944, Lev Landau noticed that near the loss of stability the amplitude of the emergent "principal motion" satisfies a very simple equation [11]. It is an example of the "bifurcational parametric simplification".

In the case of an isothermic detailed kinetics a corresponding bifurcation set for steady states multiplicity is an algebraic variety. By Whitney theorem [16] any algebraic variety admits a Whitney stratification. It is natural to conjecture that the stratum of minimal dimension corresponds to the "maximal complexity". Perhaps numerical algorithms for the Whitney stratification will be useful for an evaluation of the "maximal complexity". It seems to us that such algorithms have to be combined with a subdivision to fast and slow sub-processes.

In the applied bifurcation theory there are constructed some interesting algorithms for numerical evaluation of the stratum of minimal dimension (maximal co-dimension), see [8] and [9] that can be useful to an evaluation of the "maximal complexity" and description of many possible transition trajectories in the vicinity of critical points. It was done for isothermal chemical system [7]. Of course, such analysis of sophisticated near-steady-state behavior combined with a separation of fast and slow sub-processes looks natural. However it still does not provide with a robust knowledge on relationships between model parameters which determine this critical behavior.

1.2. Bifurcational parametric simplification of chemical kinetic models

We propose here an accurate mathematical description of the bifurcational parametric simplification for kinetic models in the case of the simplest possible bifurcation of steady states multiplicity. Our justification is based on the bifurcation theory of dynamic systems. We also use "slow-fast" dynamics, i.e. a coordinate free version of the singular perturbation theory, as a technical tool for an accurate evaluation of asymptotic analytic expressions that combine different reaction parameters [2].

The following questions play a key role in this study:

- How do the characteristics of multiple steady states and its bifurcations depend on the kinetic parameters?
- How can process properties be readily related to experimental results?

Let us explain more formally the main ideas of the bifurcational parametric simplification analysis in the case of homogeneous kinetic systems.

In the vector notation the system of governing equations of a homogeneous kinetic system can be written as

$$\frac{d\psi}{dt} = F(\psi, K)$$

where $\psi = (\psi_1, \psi_2, \dots, \psi_n)$ is the thermochemical state vector and $K = (k_1, k_2, \dots, k_s)$ is the kinetic parameter vector. (A detailed description of such models can be found in the next section.)

Suppose our model has multiple steady states $\psi_{1,s}, \psi_{2,s}, \dots, \psi_{l,s}$ that are all consistent solutions of the functional system

$$0 = F(\psi, K). \quad (1.1)$$

These steady states $\psi_{1,s}, \psi_{2,s}, \dots, \psi_{l,s}$ are functions of the kinetic parameter vector $K = (k_1, k_2, \dots, k_s)$, i.e.

$$\psi_{1,s} = g_1(K), \psi_{2,s} = g_2(K), \dots, \psi_{l,s} = g_l(K).$$

The simplest possible bifurcation is a coincidence of two steady states $\psi_{1,s} = g_1(K) = g_2(K) = \psi_{2,s}$. These bifurcations can be termed as multiplicity bifurcations. The multiplicity bifurcation happens if all coordinates of both steady states coincide, i.e. we obtain n functional/algebraic equations

$$g_1(k_1, k_2, \dots, k_s) = g_2(k_1, k_2, \dots, k_s) \quad (1.2)$$

between kinetic parameters k_1, k_2, \dots, k_s . Therefore there exists at least one functional dependence between the kinetic parameters and at most n functional dependencies. The number of independent kinetic constants I depends on the structure of the steady states system 1.1.

For this case $Q = s - I$ is the bifurcational simplification number. Any additional bifurcation point produces an additional functional equation for kinetic parameters.

The bifurcational parametric simplification with the maximal simplification number Q corresponds to a bifurcation of "maximal complexity." It is clear that in our case the maximum critical simplification is just a set of kinetic parameters. It is just a set of kinetic constants (a value $K_0 = (k_{1,0}, k_{2,0}, \dots, k_{s,0})$) for which there exists a maximal number of functional dependencies. (1.2).

Realization of the bifurcational parametric simplification analysis of kinetic systems

Here we propose an efficient and quite simple algorithm adapted to models of chemical kinetics. Main ingredients of this algorithm are:

- coordinate transformation that reverts the original model to the slow-fast one[2];
- the method of invariant manifolds for slow-fast dynamics[6];
- bifurcation analysis of invariant manifolds[6]

We apply this algorithm to the Langmuir mechanism. We corrected some inaccuracies of previous studies by Yablonsky et al using a more delicate algorithm for revealing slow-fast dynamics [2], in particular we found that the point $(0, 0)$ is not a steady-state. The main invariant of slow invariant manifolds is described as a bifurcation of "maximal complexity" of the Langmuir model.

Possible practical applications

A practical application is usually the weak point of any theoretical algorithm. We hope that experimental studies of practical systems for bifurcational kinetic parameters can help in evaluating kinetic parameters by using analytic expressions for observable quantities. These analytical expressions exist due to the bifurcational parametric simplifications phenomenon .

General Conclusions and discussion

- Any simple bifurcation point produces at least one functional dependence between kinetic parameters.
- A complex bifurcation point (for example, coincidence of more than two steady states) produces a number of functional dependencies that correspond in complexity.
- At a bifurcation point of "maximal complexity" the number of independent parameters is minimal. This means that all other kinetic parameters can be analytically recalculated.
- It is an open question as to how one can use bifurcation critical simplification for experimental study, but at least for ignition and extinction points it looks possible.

Conclusions about the Langmuir model

- All steady states, their type, stability and attraction domains are classified. Results about type and stability of steady states mainly confirm previous study [19] but are more accurate. It was proved that $(0, 0)$ is not a steady state as was claimed in [19]. Attraction domains have not been previously studied.
- All bifurcation points which are points of the multiplicity change have been studied. Similarly to [19], ignition and extinction bifurcation points have been observed. Types of these points were analyzed using the special coordinate transformation that is a subject of the theory of singular perturbed vector fields [2].
- Bifurcation parameters B_2 for ignition and B_1 for extinction were introduced and analyzed. At bifurcation points, corresponding parameters are vanishing. Bifurcation points are analyzed in details. Results are illustrated with the help of invariant slow manifolds (curves) by a number of figures.

- At the bifurcation point of “maximal complexity” both parameters are vanishing. This point provides with maximal critical simplification. This type of bifurcation, which previously was not observed or analyzed, plays a crucial role in our study.
- The first approximation of slow invariant manifold is analyzed mainly in a vicinity of the point $(0, 0)$. This analysis permits us to qualify the bifurcation type of “maximal complexity” and to evaluate reaction rates.

2. Langmuir mechanism

It is well known that the simplest mechanism for interpreting isothermal critical phenomena in heterogeneous catalysis is the Langmuir mechanism. It is a typical non-linear three-step adsorption mechanism. For CO oxidation on platinum, this mechanism is written as follows:

1. $2Z + O_2 \leftrightarrow 2ZO$;
2. $Z + CO \leftrightarrow ZCO$;
3. $ZO + ZCO \rightarrow 2Z + CO_2$.

Here Z is the free active catalyst, ZO and ZCO are species adsorbed on the catalyst surface. The first and second step are considered to be reversible.

We will divide the analysis of the problem into two parts: linear analysis (analysis of the stoichiometry matrix) and non-linear analysis (asymptotic analysis of bifurcations). The dimension of a kernel of the stoichiometric matrix give the relationship between rates of reaction; from the bifurcation analysis we obtain an additional relationship between reaction rates.

We study a more simple case of irreversible first reaction. It is valid for wide domain of concentrations and pressures [13]

1. $2Z + O_2 \rightarrow 2ZO$;
2. $Z + CO \leftrightarrow ZCO$;
3. $ZO + ZCO \rightarrow 2Z + CO_2$.

2.1. Kernel of the stoichiometric matrix

In this case the stoichiometric matrix for $x := [ZO], y := [ZCO], z := [Z]$ is

$$S = \begin{pmatrix} 2 & 0 & 0 & -1 \\ 0 & 1 & -1 & -1 \\ -2 & -1 & 1 & 2 \end{pmatrix}$$

Combining the stoichiometry matrix S with the rate reaction vector (R_1, R_2, R_{-2}, R_3) gives us the following kinetic model in terms of kinetic rates

$$\frac{dx}{dt} = 2R_1 - R_3$$

$$\frac{dy}{dt} = R_2 - R_{-2} - R_3$$

$$\frac{dz}{dt} = -2R_1 - R_2 + R_{-2} + 2R_3$$

Here $R_1 = k_1 P_{O_2} z^2$, $R_2 = k_2 P_{CO} z$, $R_{-2} = k_{-2} y$, $R_3 = k_3 x y$.

By standard calculations the rank of the stoichiometry matrix S equals two. It means that the third row of the matrix is a linear combination on the first and second rows, $Row_3 = -(Row_1 + Row_2)$. This

relation gives us the existence of a well known linear integral which relates to catalyst mass conservation low [20]

$$x + y + z = 1.$$

Because rank S is 2, the system has no other linear integrals.

Hence, the corresponding kinetic model of the open catalytic system can be reduced to

$$\frac{dx}{dt} = 2k_1P_{O_2}(1 - x - y)^2 - k_3xy$$

$$\frac{dy}{dt} = k_2P_{CO}(1 - x - y) - k_{-2}y - k_3xy.$$

This system has an invariant domain $U = [0, 1] \times [0, 1]$ in the (x, y) -phase plane.

The corresponding steady state model is:

$$2R_1 = R_3 \tag{2.1}$$

$$R_2 - R_{-2} = R_3. \tag{2.2}$$

The partial pressures P_{O_2} and P_{CO} are considered to be parameters of our model.

Conclusion. Equations (2.1) and (2.2) show that only two of four system parameters $k_1P_{O_2}, k_2P_{CO}, k_{-2}, k_3$ are independent at any steady state.

We rewrite the steady state system (2.1, 2.2) in $((x, y))$ -phase coordinates

$$2k_1P_{O_2}(1 - x - y)^2 - k_3xy = 0$$

$$k_2P_{CO}(1 - x - y) - k_{-2}y - k_3xy = 0.$$

This system has an obvious steady state solution $(1, 0)$. By simple calculations we obtain the following cubic equation for other possible steady states:

$$-2k_1P_{O_2}k_3^2x^3 + (2k_1P_{O_2}k_3^2 - 4k_1P_{O_2}k_{-2}k_3 - k_3^2k_2P_{CO})x^2$$

$$+ (4k_1P_{O_2}k_{-2}k_3 - 2k_1P_{O_2}k_{-2}^2 - k_3k_2^2P_{CO}^2 - k_{-2}k_3k_2P_{CO})x + 2k_1P_{O_2}k_{-2}^2 = 0.$$

This is a cubic equation for the variable x . Corresponding values of y can be evaluated from the previous system.

In typical catalytic processes the elementary reaction between two species on the catalytic surface x and y ($ZO + ZCO \rightarrow 2Z + CO_2$) is fast, i.e. $k_3 \gg k_1P_{O_2}, k_2P_{CO}, k_{-2}$. This permits us to introduce a small parameter $\varepsilon := 1/k_3$ and write the discriminant of the previous cubic equation in the following form:

$$\begin{aligned} & (-2k_1P_{O_2} + k_2P_{CO})^2(k_{-2}^2 - 8k_1P_{O_2}k_{-2} + 2k_2P_{CO}k_{-2} + k_2^2P_{CO}^2) - \\ & \varepsilon 4k_1P_{O_2}(24k_1^2P_{O_2}^2k_{-2}^2 + k_2P_{CO}(k_2P_{CO} + k_{-2})(2k_2^2P_{CO}^2 + 2k_2P_{CO}k_{-2} - k_{-2}^2) - \\ & \quad 2k_1P_{O_2}k_{-2}(10k_2P_{CO}^2 + k_2P_{CO}k_{-2} + k_{-2}^2)) - \\ & -\varepsilon^2 4k_1P_{O_2}^2k_2^2P_{CO}^2k_{-2}^2(-k_{-2}^2 + 8k_2^2P_{CO}^2 + 8k_{-2}(3k_1P_{O_2} + k_2P_{CO})) - \\ & -\varepsilon^3 32k_1^3P_{O_2}^3k_2^2P_{CO}^2k_{-2}^4. \end{aligned}$$

In the zero approximation $\varepsilon = 0$, the discriminant becomes very simple

$$(k_2 P_{CO} - 2k_1 P_{O_2})^2 (k_{-2}^2 - 8k_1 P_{O_2} k_{-2} + 2k_2 P_{CO} k_{-2} + k_2^2 P_{CO}^2). \quad (2.3)$$

It can be presented as a product of two terms: $k_2 P_{CO} - 2k_1 P_{O_2}$ and $k_{-2}^2 - 8k_1 P_{O_2} k_{-2} + 2k_2 P_{CO} k_{-2} + k_2^2 P_{CO}^2$. The corresponding quantities

$$\begin{aligned} B_1 &:= 1 - \frac{k_2 P_{CO}}{2k_1 P_{O_2}}; \\ B_2 &:= k_{-2}^2 - 8k_1 P_{O_2} k_{-2} + 2k_2 P_{CO} k_{-2} + k_2^2 P_{CO}^2 = \\ &= (k_2 P_{CO} + k_{-2})^2 - 8k_1 P_{O_2} k_{-2}, \end{aligned} \quad (2.4)$$

will be used later as bifurcation parameters. A bifurcation happens if $B_1 = 0$, or $B_2 = 0$. If $B_1 = B_2 = 0$, then the corresponding bifurcation has maximal complexity.

3. Transformation of the Langmuir system to a slow-fast system

The fast reaction rate $k_3 xy$ is presented in both equations. The original system does not have any fast-slow division in the original coordinate system (x, y) .

By the main concept in the theory of singularly perturbed vector fields [2], [3], it is possible to construct another orthogonal coordinate system where the original model becomes a slow-fast one. In the case of the Langmuir system it is only a simple rotation.

An obvious candidate to a small parameter is $\varepsilon := 1/k_3$. We use the following orthogonal coordinates transformation

$$\begin{aligned} u &= \frac{x - y}{\sqrt{2}}, \\ v &= \frac{x + y}{\sqrt{2}}. \end{aligned}$$

With respect to the new coordinates, the system has the form

$$\begin{aligned} \frac{du}{dt} &= \sqrt{2} k_1 P_{O_2} (1 - \sqrt{2}v)^2 - \frac{k_2}{\sqrt{2}} P_{CO} (1 - \sqrt{2}v) + \frac{k_{-2}}{2} (v - u), \\ \varepsilon \frac{dv}{dt} &= \frac{u^2 - v^2}{\sqrt{2}} + \frac{\varepsilon}{2\sqrt{2}} \left(4k_1 P_{O_2} (1 - \sqrt{2}u)^2 + 2k_2 P_{CO} (1 - \sqrt{2}v) - \sqrt{2}k_{-2} (v - u) \right). \end{aligned}$$

This is a standard slow-fast system (singularly perturbed system) that combines singular and regular perturbations in the second equation. The singular perturbation induces the small parameter ε before $\frac{dv}{dt}$, and the regular perturbation induces the same small parameter before the second term in the right hand side of the second equation.

3.1. Zero approximation $\varepsilon = 0$ for the singular perturbation

At this stage, all the machinery in the standard singular perturbation theory can be applied to the analysis of the system, including its decomposition to slow and fast subsystems and reduction of the near steady state dynamics to dynamics on invariant slow manifolds (slow curves in our model).

The zero approximation $\varepsilon = 0$ ($k_3 \rightarrow \infty$) of slow invariant curve is given by equating ε to zero before $\frac{dv}{dt}$ at the second equation. The slow curves equation is

$$\frac{u^2 - v^2}{\sqrt{2}} + \frac{\varepsilon}{2\sqrt{2}} \left(4k_1 P_{O_2} (1 - \sqrt{2}u)^2 + 2k_2 P_{CO} (1 - \sqrt{2}v) - \sqrt{2}k_{-2} (v - u) \right) = 0. \quad (3.1)$$

To simplify analysis of the steady states we put $\varepsilon = 0$ for the regular perturbation in this equation. The corresponding approximation of slow curves is represented by $u^2 - v^2 = 0$. It has two branches $u + v = 0$ and $u - v = 0$, or in the original coordinates $x = 0$ and $y = 0$. Both branches of the slow invariant manifold are stable (attractive).

Let us remark that the two branches $u + v = 0$ and $u - v = 0$ have an intersection point $(0, 0)$ where the last approximation is problematic. Around the point $(0, 0)$ a more accurate approximation is necessary. It is easy to check that $(0, 0)$ is not a steady state of the original system (see 2.1, 2.2). This problem is discussed in detail in Appendix 2.

In the original coordinates the branches are $x = 0$ and $y = 0$. Hence any steady state at this approximation has zero of its coordinates, and can not be used for the evaluation of the reaction rate $R_3 = k_3xy$ at any steady state, because it gives the reaction rate zero. This means that we have to use a more accurate approximation of (3.1) for $R_3 = k_3xy$. We shall use the steady state relationships of reaction rates (2.1, 2.2) for evaluations of R_3 .

3.2. Multiplicity of bifurcation parameters

I) For the first branch $v = u$ or $y = 0$ of the slow curve the multiplicity bifurcation parameter is

$$B_1 = 1 - \frac{k_2 P_{CO}}{2k_1 P_{O_2}}$$

(see 2.4).

There are only one or two steady states on the branch $v = u$ or $y = 0$ in the original coordinate system. The first one is $(1, 0)$ and does not depends on B_1 .

The second one is

$$\left(1 - \frac{k_2 P_{CO}}{2k_1 P_{O_2}}, 0\right).$$

If $B_1 > 0$ this steady state is stable. If $B_1 < 0$ then the second steady state does not belong to the invariant domain U , i.e it has no physical meaning. The bifurcation value of B_1 is equal 0, i.e in the bifurcation point

$$k_2 P_{CO} = 2k_1 P_{O_2}. \quad (3.2)$$

Conclusion. At the bifurcation point $B_1 = 0$, the parameters $k_1 P_{O_2}$ and $k_2 P_{CO}$ are dependent. This dependence is a bifurcational simplification. The change of sign B_1 from positive to negative corresponds to extinction, that follows from the evaluation of the reaction rates (next subsection).

II) For the second branch $v = -u$ or $x = 0$ of the slow curve the multiplicity bifurcation parameter is

$$B_2 = (k_{-2})^2 + 2k_{-2} (k_2 P_{CO} - 4k_1 P_{O_2}) + (k_2 P_{CO})^2$$

(see 2.4).

Let us remark that parameters B_1 and B_2 are not completely independent. By simple calculation we obtain that $B_2 = (k_{-2})^2 + 2k_{-2} (-4k_1 P_{O_2} B_1 - k_2 P_{CO}) + (k_2 P_{CO})^2 = (k_2 P_{CO} - k_{-2})^2 - 8k_{-2} k_1 P_{O_2} B_1$. From this relation we conclude that if $B_1 < 0$, then $B_2 > 0$ and if $B_1 = 0$ we have $B_2 = (k_2 P_{CO} - k_{-2})^2 \geq 0$, and the situation $B_1 < 0, B_2 < 0$ is not possible.

There exist two, one or zero steady states on this branch, depending on the sign of B_2 . For $B_2 < 0$ steady states does not exist. Existence of one steady states corresponds to $B_2 = 0$. For $B_2 > 0$ there exist two steady states on $x = 0$. Let us remark that k_{-2} is the leading kinetic parameter, because for $k_{-2} = 0$ the bifurcation parameter B_2 is always positive and the bifurcation does not exists.

Conclusion. At the bifurcation point $B_2 = 0$ there exists a functional relation between parameters $k_1 P_{O_2}$, $k_2 P_{CO}$, k_{-2} . It is a bifurcational simplification as well. The change in the sign of B_2 from positive to negative corresponds to ignition, that follows from the evaluation of the reaction rates (next subsection).

3.3. Calculation of reaction rates

We calculate the reaction rates at the steady states on the first slow curve $y = 0$ using the zero approximation for R_1 and R_2 and the steady state relations between rates $R_3 = 2R_1$ and $R_3 = R_2 - R_{-2}$ for the evaluations of R_3 and R_{-2} .

We use the following standard representation of the steady states coordinate x_s, y_s based on the regular perturbation theory:

$$(x_s = x_0 + \varepsilon x_1 + \dots, y_s = y_0 + \varepsilon y_1 + \dots).$$

Hence $R_3 = \frac{1}{\varepsilon}((x_0 + \varepsilon x_1 + \dots)(y_0 + \varepsilon y_1 + \dots))$. In zero approximation $\varepsilon = 0$ we have $x_0 = 0$ or $y_0 = 0$. Therefore $R_3 = x_1 y_0$ or $R_3 = x_0 y_1$.

The first branch of the slow curve is $y = 0$.

At the steady state $(1, 0)$ all reaction rates equal zero. The second steady state

$$\left(1 - \frac{k_2 P_{CO}}{2k_1 P_{O_2}}, 0\right)$$

exists for $B_1 > 0$. At this steady state the reaction rates are

$$R_1 = \frac{k_2^2 P_{CO}^2}{4k_1 P_{O_2}},$$

$$R_2 = \frac{k_2^2 P_{CO}^2}{2k_1 P_{O_2}},$$

$$R_{-2} = 0,$$

$$R_3 = 2R_1 = \frac{k_2^2 P_{CO}^2}{2k_1 P_{O_2}}.$$

Clearly, we have an equality

$$2R_1 = R_2 - R_{-2}$$

In this approximation the rate of the second reverse reaction at the first branch is zero. Hence all reactions of the detailed mechanism can be considered to be irreversible.

Remark. In the first regular approximation $(x_0 + \varepsilon x_1)$, at the first branch the rate of CO desorption (the second reverse reaction) is zero. But for more accurate approximations it is positive, but small enough. Our approximation is of the order $O(\varepsilon)$ for singular perturbations.

The second branch of the slow curve is $x = 0$.

At the case $B_2 > 0$. There exist two steady states (on this branch):

$$\left(0, 1 - \frac{k_{-2} + k_2 P_{CO} \pm \sqrt{B_2}}{4k_1 P_{O_2}}\right).$$

Corresponding reaction rates are:

$$R_1 = k_1 P_{O_2} \left(\frac{k_{-2} + k_2 P_{CO} \pm \sqrt{B_2}}{4k_1 P_{O_2}}\right)^2,$$

$$R_2 = k_2 P_{CO} \left(\frac{k_{-2} + k_2 P_{CO} \pm \sqrt{B_2}}{4k_1 P_{O_2}} \right),$$

$$R_{-2} = k_{-2} \left(1 - \frac{k_{-2} + k_2 P_{CO} \pm \sqrt{B_2}}{4k_1 P_{O_2}} \right),$$

$$R_3 = 2R_1 = 2k_1 P_{O_2} \left(\frac{k_{-2} + k_2 P_{CO} \pm \sqrt{B_2}}{4k_1 P_{O_2}} \right)^2.$$

The equation $2R_1 = R_2 - R_{-2}$ is also valid for the second branch of the slow curve.

Bifurcation points.

Now we will calculate the steady-state reaction rates at the bifurcation points.

At the first bifurcation point $B_1 = 0$ (extinction point) the reaction rates for the branch $y = 0$ are:

$$R_1 = k_1 P_{O_2},$$

$$R_2 = 2k_1 P_{O_2},$$

$$R_{-2} = 0,$$

$$R_3 = 2R_1 = 2k_1 P_{O_2}.$$

After this bifurcation the system "jumps" to the stable steady state on the branch $x = 0$. The condition $B_1 = 0$ is fulfilled at the reaction rate $2k_1 P_{O_2} \left(\frac{k_{-2} + k_2 P_{CO} - \sqrt{B_2}}{4k_1 P_{O_2}} \right)^2$ after the extinction point. Thus, the main reaction rate of R_3 at this steady state is

$$R_{3,1} = \frac{(k_{-2})^2}{2k_1 P_{O_2}}.$$

Because R_3 "jumps" from the larger value $2k_1 P_{O_2}$ to the smaller value $\frac{(k_{-2})^2}{2k_1 P_{O_2}}$ this bifurcation point is *the extinction point*, i.e it "jumps" from the extinction value R_A to the "after extinction" value R_B . By previous calculations

$$R_A R_B = (k_{-2})^2. \quad (3.3)$$

At the second bifurcation point $B_2 = 0$ (i.e. $(k_2 P_{CO} + k_{-2})^2 = 8k_{-2} k_1 P_{O_2}$) reaction rates for the branch $x = 0$ are:

$$R_1 = \frac{k_{-2}}{2},$$

$$R_2 = \frac{k_2 P_{CO}}{4k_1 P_{O_2}} (k_{-2} + k_2 P_{CO}) = \frac{k_2 P_{CO}}{4k_1 P_{O_2}} \sqrt{8k_1 P_{O_2} k_{-2}},$$

$$R_{-2} = \frac{k_{-2}}{4k_1 P_{O_2}} (4k_1 P_{O_2} - (k_{-2} + k_2 P_{CO})) = \frac{k_{-2}}{4k_1 P_{O_2}} \left(4k_1 P_{O_2} - \sqrt{8k_1 P_{O_2} k_{-2}} \right),$$

$$R_3 = 2R_1 = k_{-2}.$$

After this bifurcation the system "jumps" to the stable steady state on the branch $y = 0$. The main reaction rate R_3 at this steady state is

$$R_{3,1} = \frac{k_2^2 P_{CO}^2}{2k_1 P_{O_2}}.$$

Because R_3 "jumps" from the smaller value k_{-2} to the bigger value $\frac{k_2^2 P_{CO}^2}{2k_1 P_{O_2}}$ this bifurcation point is *the ignition point*, i.e it "jumps" from the ignition value R_C to the after ignition value R_D . By previous calculations

$$R_C R_D = \frac{k_{-2} k_2^2 P_{CO}^2}{2k_1 P_{O_2}}. \quad (3.4)$$

At the bifurcation point of the maximal complexity $B_1 = B_2 = 0$ we have a further simplification:

$$R_3 = k_{-2} = k_2 P_{CO} = 2k_1 P_{O_2}.$$

4. Dynamics of Langmuir system

In all figures, straight lines represent the zero approximation $\varepsilon = 0$, dashed lines represent the first approximation, thick points are steady states, and small arrows represent system trajectories. All figures are produced by the computer program "Mathematica".

By standard stability analysis we have that for $B_1 > 0$ and $B_2 > 0$ the steady states of $(1, 0)$ and

$$\left(0, 1 - \frac{k_{-2} + k_2 P_{CO} + \sqrt{B_2}}{4k_1 P_{O_2}}\right)$$

are saddle points. The steady states of $\left(1 - \frac{k_2 P_{CO}}{2k_1 P_{O_2}}, 0\right)$ and

$$\left(0, 1 - \frac{k_{-2} + k_2 P_{CO} - \sqrt{B_2}}{4k_1 P_{O_2}}\right)$$

are stable (attractive) nodes.

If the initial conditions satisfy the following inequality:

$$x < y - 1 + \frac{k_{-2} + k_2 P_{CO} + \sqrt{B_2}}{4k_1 P_{O_2}}$$

all trajectories are attracted to the node

$$\left(0, 1 - \frac{k_{-2} + k_2 P_{CO} - \sqrt{B_2}}{4k_1 P_{O_2}}\right).$$

For any other initial conditions all trajectories are attracted to the node

$$\left(1 - \frac{k_2 P_{CO}}{2k_1 P_{O_2}}, 0\right)$$

(see Figure 1).

In the case $B_1 > 0$, $B_2 < 0$ there are two steady states on the branch $y = 0$ and no steady state on the branch $x = 0$. Hence, all trajectories are attracted to the node

$$\left(1 - \frac{k_2 P_{CO}}{2k_1 P_{O_2}}, 0\right).$$

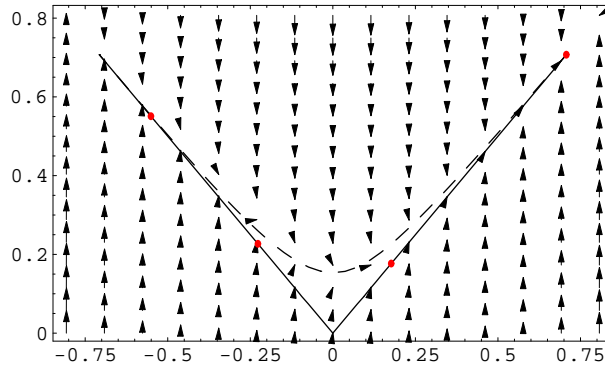


FIGURE 1. Dynamics of the system in the case $B_1 > 0, B_2 > 0$. Solid line: zero approximation of slow manifold, dotted line: first approximation of slow manifold, red points: steady states.

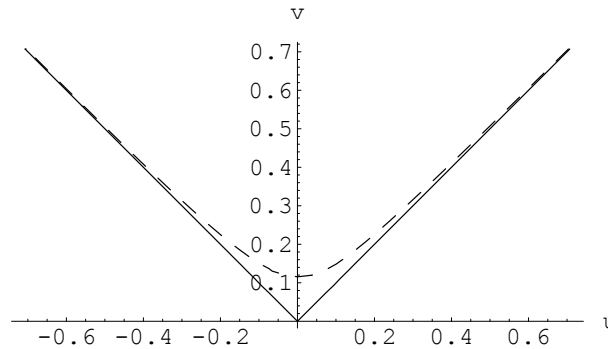


FIGURE 2. Dynamics of the system in the case $B_1 > 0, B_2 < 0$. Solid line: zero approximation of slow manifold, dotted line: first approximation of slow manifold, red points: steady states.

(see Figure 2).

In the case $B_1 < 0, B_2 > 0$ the steady state is

$$\left(0, 1 - \frac{k_{-2} + k_2 P_{CO} + \sqrt{B_2}}{4k_1 P_{O_2}} \right),$$

and it does not belong to the invariant domain U . Hence we have only two steady states.

The first one $(1, 0)$ is a saddle point, while the second one is a stable node

$$\left(0, 1 - \frac{k_{-2} + k_2 P_{CO} - \sqrt{B_2}}{4k_1 P_{O_2}} \right).$$

All trajectories are attracted to the second point (see Figure 3).

In bifurcation cases where one or both parameters B_1, B_2 become zero more accurate approximations are necessary and such analyses are beyond the scope of the zero approximation.

Conclusion. If $B_2 > 0$ and the sign of the bifurcation parameter B_1 is changed from the positive to negative one, the reaction rate R_3 decreases dramatically from large to small values (compare figures 1 and 3). It means that $B_1 = 0$ corresponds to the extinction point.

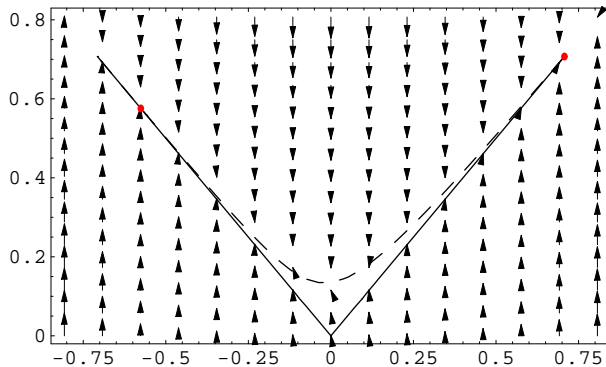


FIGURE 3. Dynamics of the system in the case $B_1 < 0$, $B_2 > 0$. Solid line: zero approximation of slow manifold, dotted line: first approximation of slow manifold, red points: steady states.

If $B_1 > 0$ and the sign of the bifurcation parameter B_2 is changed from the positive to negative one, the reaction rate R_3 make a "jump" from small to larg values (compare figures 2 and 3). This means that $B_2 = 0$ corresponds to the ignition point.

It is shown that the point of maximal bifurcation complexity present a coincidence of ignition and extinction points."

5. About the phisyc-chemical meaning of bifurcation parameters and bifurcations conditions

We follow chapter 9 of Marin and Yablonsky's book [13].

The condition $B_1 = 0$ is equivalent to $z = \frac{k_2 P_{CO}}{2k_1 P_{O_2}} = 1$ for the corresponding steady state, i.e. the entire catalyst surface is empty at the steady state. Therefore, the bifurcation parameter $B_1 := 1 - \frac{k_2 P_{CO}}{2k_1 P_{O_2}}$ determines the difference between the complete concentration of catalytic sites, i.e.,unity, and the corresponding steady-state concentration of the empty catalytic sites.

The condition $B_2 = 0$ can be reformulated in terms of the parameter

$$H := \frac{(k_2 P_{CO} + k_{-2})^2}{8k_1 P_{O_2} k_{-2}}. \quad (5.1)$$

The condition $B_2 = 0$ is equivalent to $H = 1$.

By the previous analysis the condition $B_1 = 0$ determines the extinction point and the condition $B_2 = 0$ or $H = 1$ determines the ignition point.

Detailed explanations of the condition $H = 1$ can be found in the book ([13], chapter 9). We repeat here these arguments. "At the ignition point, the steady state reaction rate $R_3 = k_3 xy$ is determined only by the CO desorption rate coefficient. It does not depend on the composition of the gas-phase mixture." At the ignition point the concentration z_{ig} of active sites is equivalent to $2z_{eq}$, where z_{eq} is an equilibrium concentration of free active sites. Let us discuss in more detail the concept of equilibrium concentration. Suppose that in our system we have only one reversible adsorption step, i.e. an interaction between the empty catalytic sites and gaseous CO . Then at the equilibrium which in this case is the steady state as well

$$k_2 P_{co} z_{eq} = k_{-2} y_{eq}.$$

From these equations, obviously

$$z_{eq} = \frac{k_{-2}}{k_2 P_{CO} + k_{-2}} = \frac{1}{K_{eq,2} P_{CO} + 1},$$

where $K_{eq,2}$ is the equilibrium constant of CO adsorption.

Before ignition, the steady state concentration of adsorbed oxygen, x is very low, therefore in the vicinity of ignition we approximately have

$$y = 1 - z_{ign} = 1 - 2z.$$

At the point of the maximal bifurcational complexity both conditions $B_1 = 0$ and $H = 1$ are fulfilled. It means that at this point **two phenomena, ignition and extinction, merge**. All the catalyst sites are empty. Using $z = 2z_{eq} = 1$, we have

$$z_{eq} = \frac{2}{K_{eq,2} P_{CO} + 1} = 1$$

and $K_{eq,2} P_{CO} = 1$.

The same equation can be obtained in a more standard way, because at the point of the maximal bifurcational complexity (MBC-point) ignition and extinction are merged, and the following equation is valid

$$R_{ext} = R_{ign}$$

where R_{ext} and R_{ign} are reaction rates at ignition and extinction points respectively. Consequently $k_{-2} = k_2 P_{CO}$ and $K_{eq,2} P_{CO} = 1$.

The last equation is quite interesting. It is nothing but the 'degenerate' Langmuir equation in the limit case when all the catalytic surface is covered by CO (rather to say almost covered).

This equation gives a unique possibility to estimate K_{eq} based just on the MBC -point experimentally observed:

$$K_{eq,2} = 1/P_{CO,MBC},$$

where $P_{CO,MBC}$ is the partial pressure of CO at the MBC -point.

Remark Distinguishing the well-observed and ill observed critical characteristics and parameters.

In catalytic CO oxidation over the Pt catalyst, the reaction rates at ignition and extinction points are ill -observed, but the after-ignition and after-extinction points are well-observed. It is possible to find reaction rates of the ill-defined points (ignition and extinction) and parameters of adsorption steps based on the information regarding the well-defined points (after-ignition and after-extinction).

6. Conclusions

A phenomenon of the bifurcational parametric simplification was presented as a generalization and a justification of the critical simplification principle described in [20]. The parametric simplification was applied to the Langmuir model using its transformation to the slow-fast dynamic system based on the concept of singularly perturbed vector fields [2]. A detailed analysis of the Langmuir model was performed, and a bifurcation of the maximum complexity was presented as a new peculiarity in terms of kinetic parameters.

Appendix 1. Mathematical models and the structure of chemical reaction mechanisms

Additional definitions of the chemical source term are required for the exposition. A pure homogeneous system is considered. It is represented by a system of ordinary differential equations (ODEs) that describes the mechanism of chemical kinetics by a system based on the mass action law.

The mathematical model describes the temporal evolution of chemical state vector, where ψ_j represents a concentration of the its chemical substance. A dimension of the system is the number of species (reactants), n_s :

$$\psi = (\psi_1, \dots, \psi_{n_s})^T.$$

In vector notation the system of governing equations of a homogeneous system can be written in autonomous form as (see e.g. [10, 17, 18])

$$\frac{d\psi}{dt} = F(\psi), \quad \psi \in \Omega \subset R^n. \quad (6.1)$$

Here the so called chemical source F represents the chemical mechanism: n_s reactants participate in n_r elementary chemical reactions. Pressure and enthalpy are considered to be constant.

The elementary reactions are

$$i = 1, \dots, n_r : \alpha_{1,i}A_1 + \dots + \alpha_{n_s,i}A_{n_s} \leftrightarrow \beta_{1,i}A_1 + \dots + \beta_{n_s,i}A_{n_s} \quad (6.2)$$

where A_1, \dots, A_{n_s} chemical species which participate in n_r elementary reactions. Reaction rates of these reactions relate to the mass action law which was already mentioned [7]. This law implies the polynomial form

$$R_i(\psi) := k_i^+ \prod_{j=1}^{n_s} \psi_j^{\alpha_{j,i}} - k_i^- \prod_{j=1}^{n_s} \psi_j^{\beta_{j,i}} \quad i = 1, \dots, n_r. \quad (6.3)$$

The rate constants k_i^+ , k_i^- are characterized by exponential Arrhenius dependences on the temperature.

Therefore, components of $F(\psi)$ are composed in the following way

$$F_j(\psi) = \sum_{i=1}^{n_r} \gamma_{j,i} R_i(\psi), \quad (6.4)$$

where $\gamma_{j,i} := \beta_{j,i} - \alpha_{j,i}$ are components of the so-called stoichiometric coefficient ($n_s \times n_r$) matrix S , and $R(\psi)$ is a non-linear vector function of the elementary reaction rates.

A specific structure of models of chemical kinetics is discussed now. The structure is based on the stoichiometric matrix S . It is typical in chemical kinetics that the number of reactions is much larger then the number of species i.e. $n_r \gg n_s$ and S is a rectangular matrix of a linear mapping from the reaction space R^{n_r} to the system state space R^{n_s} . The vector of elementary reaction rates $R(\Psi)$ is a non-linear map from the state space R^{n_s} to the reaction space R^{n_r} . Their composition represents the chemical source term (vector) $F(\Psi)$ that maps the state space R^{n_s} into itself.

This special structure of kinetic models (6.1) - (6.4) can be illustrated by the following diagram

$$\begin{array}{ccc} & R^{n_r} & \\ & R(\Psi) & \\ & \nearrow & \downarrow S \\ R^{n_s} & \longrightarrow & R^{n_s} \\ & F(\Psi) & \end{array}$$

The initial linear reduction procedure is possible for the linear map represented by the matrix S . Denote by

$$\ker S = \{w \in R^{n_r} | S(w) = 0\}$$

the kernel of the linear map $S : R^{n_r} \rightarrow R^{n_s}$. It is clear that $\dim(\ker S) \geq n_r - n_s$. If $\dim(\ker S) > n_r - n_s$, then there exist

$$q = \dim(\ker S) - (n_r - n_s) > 0$$

linear integrals in the original system. Hence, without loss of generality, the first $n_s - q$ lines of $S := \|\gamma_{j,i}\|$ can be assumed to be linearly independent, while the q lines $k = n_s - q + 1, \dots, n_s$ are linearly dependent

$$\gamma_{k,\cdot} = \sum_{\alpha=1}^{n_s-q} \sigma_{k,\alpha} \gamma_{\alpha,\cdot}$$

As the result, the following linear integrals of the original system can be found, given by the $(q \times n_s)$ matrix

$$\tilde{Z}_c = \begin{pmatrix} \sigma_{1,1} & \dots & \sigma_{1,n_s-q} & -1 & 0 & \dots & 0 \\ \sigma_{2,1} & \dots & \sigma_{2,n_s-q} & 0 & -1 & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \sigma_{q,1} & \dots & \sigma_{q,n_s-q} & 0 & 0 & \dots & -1 \end{pmatrix},$$

$$\tilde{Z}_c \cdot S \equiv 0,$$

which means \tilde{Z}_c defines the conserved quantities of the system

$$\tilde{Z}_c \cdot \frac{d\psi}{dt} = \tilde{Z}_c \cdot F(\psi) = \tilde{Z}_c \cdot S \cdot R(\psi) = 0,$$

i.e.

$$\tilde{Z}_c \cdot (\psi - \psi^0) = 0.$$

This procedure permits us to reduce the dimension of the system using the linear integrals which typically have a simple physic-chemical meaning corresponding to conserved quantities of chemical elements.

A detailed study of $\ker S$ has a long history. It is known as the ‘‘methabolic pathway analysis of null space of stoichiometric matrix’’ (see, for example, [4]). A more detailed analysis of linear-algebraic approaches with help of molecular and Horiuti matrices can be found in [5].

Steady states Ψ_1, \dots, Ψ_m of this model are solutions of the following analytic equation

$$F(\Psi_i) = 0, i = 1, 2, \dots, m.$$

Its coordinates are functions of main system parameters. Therefore, the linear integrals produce functional dependencies between main model parameters. Solving these functional dependencies we reduce number of main independent parameters by the number of the linear integrals. Typically explicit solutions of the steady state equations and its consequences for main system parameters, have a very complicated analytic nature because of the high non-linearity of the original models.

It is a first step of the parametric critical simplification.

The second step of the parametric critical simplification is connected with bifurcations. The notion of a bifurcation is not completely formal. In the case of steady state multiplicity, it means coincidence of two different steady states i.e. $\Psi_i = \Psi_j, i \neq j$. It gives an additional functional dependence between the main parameters of the model and therefore permits us to reduce at least one independent parameter. Because bifurcation typically has a simple physical meaning (ignition or extinction points, appearance of oscillations etc.) it permits us to check values of leading parameters experimentally.

Appendix 2. About the first approximation of the slow invariant curve

Recall that in u, v -coordinates the Langmuir system has the form

$$\begin{aligned}\frac{du}{dt} &= \sqrt{2}k_1P_{O_2}(1 - \sqrt{2}v) - \frac{k_2}{\sqrt{2}}P_{CO}(1 - \sqrt{2}v)^2, \\ \varepsilon \frac{dv}{dt} &= \frac{u^2 - v^2}{\sqrt{2}} + \frac{\varepsilon}{2\sqrt{2}} \left(4k_1P_{O_2}(1 - \sqrt{2}u)^2 + 2k_2P_{CO}(1 - \sqrt{2}v) \right).\end{aligned}$$

Because the zero approximation $\varepsilon = 0$ is not informative at the intersection point $(0, 0)$ of the two branches $u = v$ and $u = -v$, we calculate the first approximation of the slow curve. It is

$$u^2 - v^2 + \varepsilon \left(k_2P_{CO}(1 - \sqrt{2}v)^2 \frac{u+v}{v} + 2k_1P_{O_2}(1 - \sqrt{2})^2 \frac{v-u}{v} \right) = 0$$

(see Figure 4).

We give here a short sketch of the first approximation of steady state multiplicity. We do not present here all of the long elementary calculations, but focus rather on the vicinity of the problematic intersection point $(0, 0)$. Far from $(0, 0)$ the first approximation loses its corrective influence on the results.

The first bifurcation parameter B_1 in the first approximation becomes

$$B_{1,1} = \left(1 - \frac{k_2P_{CO}}{2k_1P_{O_2}} \right)^2 - \varepsilon \frac{2k_2^2P_{CO}^2}{k_1P_{O_2}}.$$

Depending on this bifurcation parameter the system has four, three or two steady states. Existence of three steady states $((0, 1), (1, 0)$ and

$$\left(\frac{1}{2} \sqrt{\varepsilon \frac{2k_2^2P_{CO}^2}{k_1P_{O_2}}}, \frac{1}{2} \sqrt{\varepsilon \frac{2k_2^2P_{CO}^2}{k_1P_{O_2}}} \right)$$

corresponds to $B_{1,1} = 0$. The third steady state

$$\left(\frac{1}{2} \sqrt{\varepsilon \frac{2k_2^2P_{CO}^2}{k_1P_{O_2}}}, \frac{1}{2} \sqrt{\varepsilon \frac{2k_2^2P_{CO}^2}{k_1P_{O_2}}} \right)$$

belongs to an ε -vicinity of $(0, 0)$. For $\varepsilon \rightarrow 0$ this point disappears from the vicinity of the $(0, 0)$ point. This steady state disappears for $B_{1,1} < 0$.

The first order approximation of the slow manifold is presented at Figure 4.

In the invariant domain we have that $k_2P_{CO}(1 - \sqrt{2}v)^2 \frac{u+v}{v} + 2k_1P_{O_2}(1 - \sqrt{2})^2 \frac{v-u}{v} > 0$. This inequality leads to the conclusion that non trivial steady states lie inside the invariant domain. In the case $B_{1,1} = 0$ two non trivial steady states come together and we obtain one steady state that it is a saddle-node. In this case, if the initial condition satisfies the inequality: $x < y$, all trajectories attract to the $(0, 1)$ point. If the initial condition satisfies the inequality $x > y$, all trajectories attract to the $\left(\frac{1}{2} \sqrt{\varepsilon \frac{2k_2^2P_{CO}^2}{k_1P_{O_2}}}, \frac{1}{2} \sqrt{\varepsilon \frac{2k_2^2P_{CO}^2}{k_1P_{O_2}}} \right)$ point.

The case of $B_1 = 0, B_2 = 0$ is more complex and the standard asymptotic analysis is not applicable. Actually, this case is more interesting because this bifurcation point is the point of the maximal simplification of the system. At this point we obtain that $k_{-2} = k_2P_{CO} = 2k_1P_{O_2}$.

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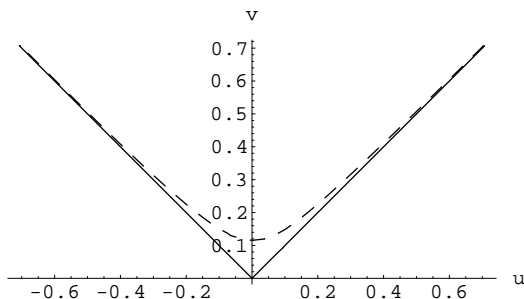


FIGURE 4. Solid line: zero approximation of slow manifold, dotted line: first approximation of slow manifold

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