CHAPTER 2

Overall Reaction Rate Equation of Single-Route Complex Catalytic Reaction in Terms of Hypergeometric Series

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Advances in Chemical Engineering, Volume 34
ISSN 0065-2377, DOI 10.1016/S0065-2377(08)00002-1

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Abstract

The non-linear theory of steady-steady (quasi-steady-state/pseudo-steady-state) kinetics of complex catalytic reactions is developed. It is illustrated in detail by the example of the single-route reversible catalytic reaction. The theoretical framework is based on the concept of the *kinetic polynomial* which has been proposed by authors in 1980–1990s and recent results of the algebraic theory, i.e. an approach of hypergeometric functions introduced by Gel'fand, Kapranov and Zelevinsky (1994) and more developed recently by Sturnfels (2000) and Passare and Tsikh (2004). The concept of ensemble of *equilibrium subsystems* introduced in our earlier papers (see in detail Lazman and Yablonskii, 1991) was used as a physico-chemical and mathematical tool, which generalizes the well-known concept of "equilibrium step". In each equilibrium subsystem, (*n*—1) steps are considered to be under equilibrium conditions and one step is limiting (*n* is a number of steps of the complex reaction). It was shown that *all solutions* of these equilibrium subsystems define coefficients of the *kinetic polynomial*.

As a result, it was obtained an analytical expression of the reaction rate in terms of hypergeometric series with *no classical simplifications about the "limiting step" or the "vicinity of the equilibrium"*. The obtained explicit equation, "four-term equation", can be presented as follows in the Equation (77):

$$R = \frac{k_{+}\left(f_{+}(c) - K_{\mathrm{eq}}^{-1} f_{-}(c)\right)}{\sum(k,c)} \quad N(k,c)$$

It has four terms:

(1) *an apparent kinetic coefficient* k_+; (2) *a "potential term"* $(f_+(c) - K_{eq}^{-1} f_-(c))$ related to the net reaction ("driving force" of irreversible thermodynamics); (3) a *"resistance" term,* $\Sigma(k,c)$, denominator of the polynomial type, which reflects complexity of chemical reaction, both its non-elementarity (many-step character) and non-linearity of elementary steps as well; (4) finally, *the "fourth term"*, $N(k,c)$. This fourth term is generated exclusively by the non-linearity of reaction steps. This term is the main distinguishing feature of this equation in comparison with Langmuir–Hinshelwood–Hougen–Watson (LHHW) equations based on simplifying assumptions. In absence of non-linear steps the "fourth" term is also absent.

It was demonstrated that the hypergeometric rate representation covers descriptions, which correspond to typical simplifications ("vicinity of the equilibrium", "rate-limiting step").

Using kinetic models of typical catalytic mechanisms (Eley–Rideal and Langmuir–Hinshelwood (LH) mechanisms) as examples, we found parametric domains, in which the hypergeometric representation is an excellent approximation of the exact solution. Unexpectedly, this representation works well even very far from the equilibrium in the small rate domain (*low-rate branch*). Convergence problems of the hypergeometric representation have been discussed.

The obtained results can be used for a description of kinetic behavior of steady-state open catalytic systems as well as quasi (pseudo)-steady-state catalytic systems, both closed and open.

1. INTRODUCTION

A single-route complex catalytic reaction, steady state or quasi (pseudo) steady state, is a favorite topic in kinetics of complex chemical reactions. The practical problem is to find and analyze a steady-state or quasi (pseudo)-steady-state kinetic dependence based on the detailed mechanism or/and experimental data. In both mentioned cases, the problem is to determine the concentrations of intermediates and *overall reaction rate* (i.e. rate of change of reactants and products) as dependences on concentrations of reactants and products as well as temperature. At the same time, the problem posed and analyzed in this chapter is directly related to one of main problems of theoretical chemical kinetics, i.e. search for general law of complex chemical reactions at least for some classes of detailed mechanisms.

By definition of the steady-state regime, the steady-state rate of change of the intermediate concentrations equals zero.

As for the quasi (pseudo)-steady-state case, the basic assumption in deriving kinetic equations is the well-known Bodenshtein hypothesis according to which the rates of formation and consumption of intermediates are equal. In fact, Chapman was first who proposed this hypothesis (see in more detail in the book by Yablonskii et al., 1991). The approach based on this idea, the Quasi-Steady-State Approximation (QSSA), is a common method for eliminating intermediates from the kinetic models of complex catalytic reactions and corresponding transformation of these models. As well known, in the literature on chemical problems, another name of this approach, the Pseudo-Steady-State Approximation (PSSA) is used. However, the term "Quasi-Steady-State Approximation" is more popular. According to the Internet, the number of references on the QSSA is more than 70,000 in comparison with about 22,000, number of references on PSSA.

All our analysis is done under the assumption that chemical kinetics is the limiting factor of the complex chemical process, not transport of reactants/products.

The original model regarding surface intermediates is a system of ordinary differential equations. It corresponds to the detailed mechanism under an assumption that the surface diffusion factor can be neglected. Physico-chemical status of the QSSA is based on the presence of the 'small parameter', i.e. the total amount of the surface active sites is small in comparison with the total amount of gas molecules. Mathematically, the QSSA is a zero-order approximation of the original (singularly perturbed) system of differential equations by the system of the algebraic equations (see in detail Yablonskii et al., 1991). Then, in our analysis we simply replace the differential equations of the "fast" catalytic intermediates by the corresponding algebraic equations.

In comparison with the linear case, the non-linear one represents much greater challenge in deriving rate as no simple explicit formula like Cramer's rule exists here. Chemists always tried to overcome the mathematical difficulties of the analysis of the non-linear detailed kinetic model introducing simplifying hypotheses such as a hypothesis on existence of the single rate-limiting stage or hypothesis of the vicinity of thermodynamic equilibrium. First results here were obtained independently by Professor J. Horiuti (Japan) and Academician G.K. Boreskov (Russia). They introduced the fundamental concepts of *stoichiometric number* and *molecularity* of steps and found kinetic equations based on the limiting step assumption. Reaction rate equations grounded on these assumptions found wide area of practical application including situations far beyond the assumptions of the original theory. It has to be mentioned however that the validity of the popular assumption on the limiting step is not so trivial problem. Recently, Gorban (2005) and Gorban and Radulescu (2008) revisited the mathematical status of this classical hypothesis and found many non-trivial cases and misinterpretations as well. They rigorously studied the difference in limiting between transient and quasi-steady-state regimes and classified different scenarios of limiting in chemical kinetics. Quasi-steady-state regimes can be considered as specific invariant manifolds which general theory was developed by Gorban and Karlin (2003) and Gorban (2005).

Nevertheless, in this area, particularly in presenting explicit solutions of QSSA-kinetic models, theoretical chemical kinetics is still far from completing.

What could be done in the general non-linear case? Authors (Lazman and Yablonsky) started answering this question by applying constructive algebraic geometry. In early 1980s, we have proved that QSSA system corresponding to the single-route reaction mechanism of catalytic reaction can be reduced to a *single polynomial* in terms of reaction rate and concentrations (parameters of reactions are Arrhenius dependences of the temperature). In this case, the reaction rate of complex reaction is now *an implicit, not explicit* function of concentrations and temperature. Mathematically, this polynomial (i.e. *kinetic polynomial*) is a resultant of the QSSA algebraic system. Its vanishing is a necessary and sufficient condition for steady state. Thus, the roots of kinetic polynomial are the values of reaction rate in the steady state.

In this chapter, we will try to answer the next obvious question: can we find an *explicit* reaction rate equation for the general *non-linear* reaction mechanism, at least for its *thermodynamic branch*, which goes through the equilibrium. Applying the kinetic polynomial concept, we introduce the new *explicit* form of reaction rate equation in terms of hypergeometric series.

The second motive of this chapter is concerned with evergreen topic of interplay of chemical kinetics and thermodynamics. We analyze the generalized form of the explicit reaction rate equation of the *thermodynamic branch* within the context of relationship between forward and reverse reaction rates (we term the corresponding problem as the Horiuti–Boreskov problem). We will compare our equation with the well-known LHHW equation and demonstrate both similarities and differences.

In our approach, the concept of ensemble of equilibrium subsystems introduced in our earlier chapters (see in detail Lazman and Yablonskii, 1991) was used as a very efficient tool of mathematical analysis and physico-chemical understanding. The equilibrium subsystem is such a system that corresponds to the following assumption: ($n-1$) steps are considered to be under equilibrium conditions, one step is limiting, where n is a number of steps. In fact, the concept of ‘‘equilibrium subsystems’’ is a generalization of the concept of ‘‘equilibrium step’’, which is well known in chemical kinetics. Then, we take n of these equilibrium subsystems (*an ensemble of equilibrium subsystems*). It was shown that solutions of these subsystems (‘‘roots’’, ‘‘all roots’’, not just one ‘‘root’’) define coefficients of the *kinetic polynomial.*

We term our equation obtained for the thermodynamic branch of the reaction rate as ‘‘the four-term rate equation’’. This equation generalizes the known explicit forms of overall reaction rate equations. The mentioned terms are following: (1) *the kinetic apparent coefficient*; (2) *the potential term*, or *driving force* related to the thermodynamics of the net reaction; (3) *the term of resistance*, i.e. the denominator, which reflects the complexity of reaction, both its multi-step character and its non-linearity; finally, (4) *the non-linear term* which is caused exclusively by non-linear steps. In the case of linear mechanism, this term is vanishing. Distinguishing this fourth term is the original result of this chapter. In classical theoretical kinetics of heterogeneous catalysis (LH and Hougen—Watson (HW) equations) such term is absent.

Finally, we present the results of the case studies for Eley–Rideal and LH reaction mechanisms illustrating the practical aspects (i.e. convergence, relation to classic approximations) of application of this new form of reaction rate equation. One of surprising observations here is the fact that hypergeometric series provides the good fit to the exact solution not only in the vicinity of thermodynamic equilibrium but also far from equilibrium. Unlike classical approximations, the approximation with truncated series has non-local features. For instance, our examples show that approximation with the truncated hypergeometric series may supersede the conventional rate-limiting step equations. For thermodynamic branch, we may think of the domain of applicability of reaction rate series as the domain, in which the reaction rate is relatively small.

However, first we have to explain in detail a situation in the corresponding area of theoretical chemical kinetics and our chemico-mathematical framework.

1.1 Linear and non-linear mechanisms

Regarding the participation of intermediate in the steps of detailed mechanism, Temkin (1963) classified catalytic reaction mechanisms as linear and non-linear ones. For linear mechanisms, every reaction involves the participation of only one molecule of the intermediate substance. The typical linear mechanism is the two-step catalytic scheme (Temkin–Boudart mechanism), e.g. water–gas shift reaction:

$$\begin{array}{l} 1.\quad Z + H_2O \Leftrightarrow ZO + H_2 \\ 2.\quad ZO + CO \Leftrightarrow Z + CO_2 \\ \hline \quad \text{Overall reaction:} \\ \quad CO + H_2O \Leftrightarrow H_2 + CO_2 \end{array},$$

where Z and ZO are reduced and oxidized forms of catalyst, respectively, Boudart and Diega-Mariadassou (1984).

The typical non-linear mechanism is three-step adsorption mechanism (LH mechanism), e.g.

$$\begin{array}{l} 1.\quad O_2 + 2Pt \Leftrightarrow 2PtO \\ 2.\quad CO + Pt \Leftrightarrow PtCO \\ 3.\quad PtO + PtCO \rightarrow 2Pt + CO_2 \\ \hline \quad \text{Overall reaction:} \\ \quad 2CO + O_2 \rightarrow 2CO_2 \end{array},$$

where Pt is am empty site of platinum catalyst; PtO and PtCO are surface oxygen and CO, respectively.

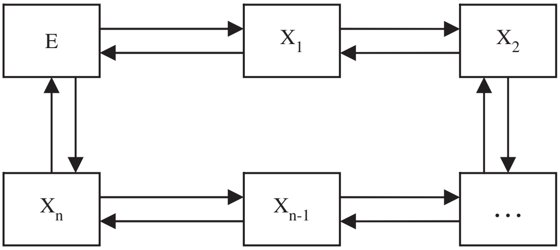
In many cases it is assumed that the rate of any elementary reaction is governed by the Mass-Action-Law (MAL). We will make the same assumption as well.

1.2 Rate equation for one-route linear mechanism

The overall rate equation of complex single-route reaction with the linear detailed mechanism was derived and analyzed in detail by many researchers. King and Altman (1956) derived the overall reaction rate equation for single-route enzyme reaction with an arbitrary number of intermediates

$$\begin{array}{l} 1.\quad S + E \Leftrightarrow X_1 \\ 2.\quad X_1 \Leftrightarrow X_2 \\ \qquad \vdots \\ n.\quad X_{n-1} \Leftrightarrow P + E. \\ \hline \text{Overall reaction:} \\ S \Leftrightarrow P \end{array}$$

using the methods of graph theory. The graph of this complex reaction was presented as



Later, in 1970s and 1980s, Evstigneev et al. (1978, 1979, 1981) systematically analyzed this equation applying methods of graph theory. They found a variety of its interesting structural properties regarding the link between kinetics of the complex reaction and structure of the reaction mechanism.

1. This equation can be always presented in the form

$$R = \frac{C}{\sum} \tag{1}$$

where R is the reaction rate and C is a cyclic characteristic;

$$C = K^{+} f^{+}(\vec{c}) - K^{-} f^{-}(\overleftarrow{c}) \tag{1a}$$

$$K^{+} = \prod_i k_i^{+}, \quad K^{-} = \prod_i k_i^{-} \tag{1b}$$

$$K^{+}/K^{-} = K_{\mathrm{eq}} \tag{1c}$$

$\vec{c}$ and $\overleftarrow{c}$ are sets of concentrations of reactants and products, respectively; k_i^{+} and k_i^{-} are Arrhenius-type kinetic constants of the forward and reverse reactions, respectively; K_{eq} is the equilibrium constant of the overall reaction.

2. The numerator C of expression (1) does not depend on the complexity of the detailed mechanism. It always corresponds to the overall reaction.
3. The denominator $\sum$, the "resistance" term, reflects the real complexity of the detailed mechanism. We can present it as

$$\sum = \sum_j K_j \prod_l c_l^{p_{jl}} \tag{2}$$

where K_j is either the product of kinetic constants of some reactions of detailed mechanism or sum of such products, c_l the concentration of reactant (product) and p_{jl} the positive integer. The physical meaning of the denominator $\sum$ is a "resistance", i.e. the "retardation" of the overall reaction rate by the intermediates of detailed mechanism. No doubt, from the energetic point of view catalytic intermediates accelerate the whole reaction decreasing the apparent activation energy. However, at the same time the complex reaction is not a "single event". It is occurred via catalytic intermediates that take a part of reacting substances.

Equation (2) can be termed as the "Langmuir form". Equation (1) can be presented in the form

$$\left(\sum\right) R - C = 0 \tag{3}$$

which is a particular case of the *kinetic polynomial* (see below).

4. We can write the rate equation (1) as a difference of forward and reverse overall rates

$$R = R^{+} - R^{-} \tag{4}$$

where

$$R^+ = \frac{K^+ f^+(\vec{c})}{\sum}, \qquad R^- = \frac{K^- f^-(\overleftarrow{c})}{\sum} \tag{5}$$

can be termed as overall reaction rates of forward and reverse reactions, respectively, and

$$\frac{R^+}{R^-} = \frac{K^+}{K^-} \frac{f^+(\vec{c})}{f^-(\overleftarrow{c})} \tag{6}$$

5. At the thermodynamic equilibrium, when $R = 0$, we have

$$R^+ = R^- \tag{7}$$

and

$$\frac{K^+}{K^-} = K_{\mathrm{eq}} = \frac{f^-(\overleftarrow{c})}{f^+(\vec{c})} \tag{8}$$

6. Different properties of Equation (1), particularly a number of independent parameters K_j (see Equation (2)) and relationships between them, the properties of apparent kinetic order (i.e. $\partial \ln R/\partial \ln c_l$) and apparent activation energy (i.e. $\partial \ln R/\partial(-1/RT)$) in terms of concentrations of intermediates and parameters of detailed mechanism have been found (see the monograph by Yablonskii et al., 1991).

Some examples of kinetic equations of complex catalytic reactions are presented in Appendix 1.

Equation (3) is linear with respect to the reaction rate variable, R. In the further analysis of more complex, non-linear, mechanisms and corresponding kinetic models, we will present the polynomial as an equation, which generalizes Equation (3), and term it as the *kinetic polynomial*. We will demonstrate that the overall reaction rate, in the general non-linear case, cannot generally be presented as a difference between two terms representing the forward and reverse reaction rates. This presentation is valid only at the special conditions that will be described.

The similar analysis for particular multi-route linear mechanism was done in 1960s by Vol'kenstein and Gol'dstein (1966) and Vol'kenstein (1967). In 1970s, the rigorous "structurized" equation for the rate of multi-route linear mechanism was derived by Yablonskii and Evstigneev (see monograph by Yablonskii et al., 1991). It reflects the structure of detailed mechanism, particularly coupling between different routes (cycles) of complex reaction. Some of these results were rediscovered many years later and not once (e.g. Chen and Chern, 2002; Helfferich, 2001).

1.3 Single route overall rate equation in applied kinetics

In remarkable progress of catalytic industry in 1930–1950s, a kinetic model was considered as a basis of reactor design. Langmuir and Hinshelwood compensated a lack of information about surface intermediates and detailed mechanism via two simple assumptions:

(i) Catalytic process is occurred by competition between the components of the reaction mixture for sites on the catalyst surface.
(ii) Adsorption and desorption rates are high in comparison to other steps of chemical transformation on the catalyst surface.

When the complex catalytic reaction is irreversible, a typical form of the corresponding kinetic equation, i.e. LH equation, is written as follows:

$$R = \frac{K\prod\limits_i c_i}{1+\sum\limits_i K_i c_i^{m_i}} \tag{9}$$

In the case of reversible reaction, Hougen and Watson proposed the similar semi-empirical equation (HW equation). For instance, for the reaction of cyclohexane dehydrogenation this equation has the form

$$R = \frac{K^+ c_{C_6H_{12}} - K^- c_{C_6H_{10}} c_{H_2}}{(K_1 c_{C_6H_{10}}^{\alpha} + K_2 c_{H_2}^{\beta} + K_3 c_{C_6H_{12}}^{\gamma})^m} \tag{10}$$

Equations (9) and (10) are called LHHW equations indicating their similarity: they belong to the class of "numerator divided by denominator" kinetic equations.

In HW equations the numerator of the expression (10) is considered to be correspondent to the overall reaction. However, within the *semi-empirical* HW approach, which was not mechanistic, the relationships between the detailed mechanisms and kinetic dependences could not be analyzed.

1.4 Relationships between forward and reverse overall reaction rates: Horiuti–Boreskov problem

Equation (10) can be presented as the difference of two terms, the forward and reverse reaction rates,

$$R = R^+ - R^- \tag{11}$$

where

$$\frac{R^+}{R^-} = K_{eq}\frac{f^+(\vec{c})}{f^-(\overleftarrow{c})} \tag{12}$$

There is a famous question posed firstly by the Japanese scientist Juro Horiuti before WWII (1939), and then, independently, by the Russian scientist Georgii Boreskov in 1945: "How to find the equation for reaction rate in back direction knowing the rate expression in a forward direction?" (detailed description of the problem is presented by Horiuti (1973), see also Boreskov's (1945) original paper).

Horiuti posed this problem and solved it only for the special example of reaction on a hydrogen electrode. Boreskov with no knowledge about the

Horiuti's results (there was a war!) analyzed the SO_2 oxidation case. Both Horiuti and Boreskov assumed that all reaction steps, except one of them, are reversible and fast. These steps are not obligatory adsorption steps. One reversible step, i.e. rate-determining one, is much slower than the rest of other steps. Using SO_2 oxidation as an example and assuming power low kinetic expressions for the reaction rates, Boreskov showed that

$$\frac{R^+}{R^-} = \left[K_{\mathrm{eq}} \frac{f^+(\vec{c})}{f^-(\overleftarrow{c})}\right]^M \tag{13}$$

and

$$R = R^+ \left\{ 1 - \left[\frac{f^-(\overleftarrow{c})}{K_{\mathrm{eq}} f^+(\vec{c})}\right]^M \right\} \tag{14}$$

where $f^+(\vec{c})$ and $f^-(\overleftarrow{c})$ are kinetic dependencies corresponding to overall reaction (forward and reverse), M a number related to the rate-determining step.[1] The rate of reverse reaction was estimated on isotope exchange data in reactions of SO_2 oxidation and ammonia synthesis. Then, the power M that Boreskov called the "molecularity" was found. For SO_2 oxidation it was 1/2.

Within the Horiuti's approach, the physical meaning of the molecularity is clear. Horiuti introduced the concept of stoichiometric numbers (*Horiuti numbers*, v).[2] Horiuti numbers are the numbers such that, after multiplying the chemical equation for every reaction step by the appropriate Horiuti number v_i and subsequent adding, all reaction intermediates are cancelled. The equation obtained is the overall reaction. In the general case, the Horiuti numbers form a matrix. Each set of Horiuti numbers (i.e. matrix column) leading to elimination of intermediates corresponds to the specific reaction route.[3]

For typical one-route linear mechanisms all the Horiuti numbers can be selected to be equal to 1.[4] This is not necessarily true for non-linear reaction mechanism, e.g. for SO_2 oxidation mechanism

$$\begin{array}{lll} 1. & 2K + O_2 \Leftrightarrow 2KO & 1 \\ 2. & KO + SO_2 \Leftrightarrow K + SO_3 & 2 \\ \hline & 2SO_2 + O_2 \Leftrightarrow 2SO_3 & \end{array} \tag{15}$$

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[1] Boreskov assumed the power law dependence for reaction rate, which is mathematically incorrect. Thus, strictly speaking, he did not prove Equations (13) and (14). Authors performed the analysis of the model corresponding to the single-route reaction mechanism with the rate-limiting step and proved these relations rigorously (see Lazman and Yablonskii, 1988; Lazman and Yablonskii, 1991). Mathematically, expression (12) is the first term of infinite power series by powers kinetic parameters of rate-limiting step.

[2] It is more convenient, in our opinion, to use the term "Horiuti number" instead of the "stoichiometric number" as the latter could be mistakenly identified with the term "stoichiometric coefficient" which designates the number of molecules participating in the reaction.

[3] Obviously, Horiuti numbers are defined up to non-singular linear transformation.

[4] They can be zero for "buffer" reaction steps (such step that involves the reaction intermediate participating in this stage exceptionally).

According to the Temkin's classification, this mechanism is non-linear, because in the first step oxygen reacts with two catalyst sites K. Numbers to the right of stoichiometric equations are Horiuti numbers: $\nu_1 = 1$ and $\nu_2 = 2$. An analysis of data by Boreskov showed that the power M in Equations (13) and (14) is

$$M = 1/\nu_{\mathrm{lim}}$$

where ν_{lim} is Horiuti number of rate limiting reaction step. Experimental data demonstrated that:

$$\frac{R^+}{R^-} = \left(K_{\mathrm{eq}} \frac{c_{\mathrm{SO_2}} c_{\mathrm{O_2}}}{c_{\mathrm{SO_3}}}\right)^{1/2}$$

Thus, $M = 1/\nu_{\mathrm{lim}} = 1/2$, $\nu_{\mathrm{lim}} = 2$ and the second step of reaction mechanism (15) is rate limiting step.

It is not still absolutely clear if the Horiuti–Boreskov representation is valid in the general case (for instance, for single-route non-linear mechanisms without rate-limiting step) and under which conditions it could be valid. It seems both scientists considered this representation is valid in all the domain of conditions. Both tried to find the relationship between R^+ and R^- considering that such distinguishing does exist always. However it is a problem! Having respect to scientists who first started to work in this area, we term it as the "Horiuti–Boreskov problem".

We formulate this problem as follows:

Under which conditions the presentation $R = R^+ - R^-$ *is valid for the complex reaction?*

2. RIGOROUS ANALYSIS OF COMPLEX KINETIC MODELS: NON-LINEAR REACTION MECHANISMS

The solution of such a problem became possible since early 1980s that was concerned with the following factors:

- increasing interest in decoding the non-linear phenomena (steady-state multiplicity, self-oscillations, etc.) and
- new mathematical results in algebraic geometry, complex analysis and computer algebra; personal motivation in solving Horiuti–Boreskov problem.

2.1 Quasi-steady-state approximation

As previously mentioned, the QSSA is a common method for eliminating intermediates from the kinetic models of complex catalytic reactions and corresponding transformation of these models. Mathematically, it is a zero-order approximation of the original (singularly perturbed) system of differential equations, which describes kinetics of the complex reaction. We simply replace the differential equations corresponding to the "fast" intermediates with algebraic equations

$$\Gamma^T \bar{w} = 0 \tag{16}$$

Let n be a number of reactions and m be a number of intermediates in the reaction mechanism. The vector $\bar{w} = (w_1, \ldots, w_n)^T$ is composed of the rates of reaction steps. Assuming the MAL, we have

$$w_i = f_i \prod_{j=1}^{m} z_j^{\alpha_{ij}} - r_i \prod_{j=1}^{m} z_j^{\beta_{ij}}, \qquad i = 1, \ldots, n \tag{17}$$

where z_j is the concentration of jth intermediate; f_i, r_i are reaction weights of forward and reverse reactions of step i.

Reaction weight is a reaction rate calculated at unit concentrations of intermediates, i.e. it is either the reaction constant or the reaction constant multiplied by power product corresponding to the "slow" components (either reagents or products). Thus, the dependencies of reaction rate on temperature and concentrations are "hidden" in reaction weights.

Non-negative integers α_{ij}, β_{ij} are stoichiometric coefficients of component j in reaction i. Matrix $\Gamma = (\gamma_{ij})$ is a stoichiometric matrix of some rank (rk), with elements $\gamma_{ij} = \beta_{ij} - \alpha_{ij}$.

Let $r = rk\Gamma$. We assume that $r < n$. In this case, there exists the $n \times P$ matrix N, such that

$$\Gamma^T \mathrm{N} = 0 \tag{18}$$

The number

$$P = n - r \tag{19}$$

is the number of *reaction routes*. Reaction route corresponds to the column of matrix N. These columns are linearly independent and form the *stoichiometric basis*. Elements of matrix N are *Horiuti numbers* ν_{sp}. The stoichiometric basis is defined up to a non-singular linear transformation. We can always define the stoichiometric basis in terms of integer stoichiometric numbers. We assume below that all ν_{sp} are integers. If we multiply each chemical equation of our mechanism by the corresponding stoichiometric number from some column of matrix N and add up the results, we obtain the chemical equation free of intermediates. This equation corresponds to the *net reaction* of the selected reaction route.

Vector $\bar{w}$ solves the homogeneous linear system (16) if and only if it belongs to the space spanned by columns of the matrix N. There exists such a vector $\bar{R} = (R_1, \ldots, R_P)^T$ that

$$\bar{w} = \mathrm{N}\bar{R} \tag{20a}$$

The element of vector $\bar{R}$ is the *rate along the reaction route*. Concentrations of intermediates satisfy $B = m - r$ linear balance equations

$$\mathbf{L}(\mathbf{z}) = 0 \tag{20b}$$

Systems (20a) and (20b)[5] of $n+B$ equations in $n+B$ unknowns $z_1, \ldots z_n$ and $R_1, \ldots R_P$, is the equivalent presentation of the original problem (16)[6]. For the single-route reaction mechanism vector $\bar{R}$ has only one element R, which is the overall reaction rate (the rate of net reaction).

2.2 Non-linear mechanisms: the kinetic polynomial

2.2.1 The resultant in reaction rate

Assuming the MAL, the system (20) consists of polynomials of variables $z_1, \ldots z_n$, and $R_1, \ldots, R_P$. Powerful techniques of effective algebraic geometry can be applied to polynomial systems. In many cases, we can apply the *variable elimination* and reduce our system to a single polynomial equation of the single variable. Mathematically, we need to find the invariant of our algebraic system, i.e. the system *resultant* (see Bykov et al., 1998; Gel'fand et al., 1994; van der Waerden, 1971 for algebraic background).

In chemical kinetics, the overall reaction rate is a natural choice for the variable. The resultant in terms of the reaction rate is a generalization of the reaction rate equations of conventional explicit form (Equation (1)) which are obtained for linear reaction mechanism. Generally, the resultant is a polynomial in terms of the overall reaction rate. The roots of this polynomial are the values of reaction rate corresponding to the solutions of the system of algebraic equations corresponding to the QSSA. It was shown before that this system (i.e. QSSA system) could be written in two equivalent forms: Equations (16) and (20). System (16) is obtained from system of differential equations of material balance of intermediates by replacing the time-derivatives of intermediate concentrations (for instance, surface coverages of intermediates in heterogeneous catalysis) with zero. System (20) is equivalent form of QSSA expressed in terms of rates $\bar{R}$ along the reaction paths.

We have termed the resultant of the overall reaction rate as the *kinetic polynomial*. Equation (3) is just the particular form of kinetic polynomial for the linear mechanism.

Authors founded the kinetic polynomial theory in early 1980s (Lazman and Yablonskii, 1991; Lazman et al., 1985a, 1985b, 1987a, 1987b; Yablonskii et al., 1982, 1983). It was further developed in collaboration with mathematicians Bykov and Kytmanov (Bykov et al., 1987, 1989).[7] Later, applying computer algebra methods,

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[5] In heterogeneous catalysis equations (20b) express the preservation of number of active cites of particular type, for instance we have $\mathbf{L}(\mathbf{z}) = z_1 + \ldots + z_m - 1$ for catalyst with single type of active cites when each of intermediates occupy one active cite.

[6] Introduction of stoichiometric number concept and linear transformation of the "conventional" QSSA equations (16) to the equivalent system (20) was essentially the major (and, possibly, only) result of theory of steady reactions developed independently by J. Horiuti in 1950s and M. I. Temkin in 1960s.

[7] Remarkably, the development of kinetic polynomial stimulated obtaining pure mathematical results that became the "standard references" in mathematical texts (see, for instance, WWW sources as E. W. Weisstein. "Resultant". From *MathWorld* — A Wolfram Web Resource. http://mathworld.wolfram.com/Resultant.html, Multidimensional logarithmic residues, Encyclopaedia of Mathematics — ISBN 1402006098 Edited by Michiel Hazewinkel CWI, Amsterdam, 2002, Springer, Berlin).

first author (Lazman) developed the kinetic polynomial software (see Bykov et al., 1993, 1998; Lazman and Yablonsky, 2004).

Kinetic polynomial found important applications including parameter estimation (Lazman et al., 1987a, Yablonskii et al., 1992), analysis of kinetic model identifiability (Lazman et al., 1987b), asymptotic analysis of bifurcations in heterogeneous catalysis (Lazman et al., 1985b; Yablonsky and Lazman, 1996, 1997; Yablonsky et al., 2003), and, of course, finding all steady states of kinetic models (Lazman, 1997, 2000, 2002, 2003a, 2003b; Lazman and Yablonsky, 2004). Detailed discussions and mathematical proofs of more technical results have been presented in the paper by Lazman and Yablonskii (1991) and book by Bykov et al. (1998).

We studied the following system (let us call it the *Basic Case*) corresponding to the single-route mechanism of catalytic reaction with the single type of active sites

$$w_s(z_1,\ldots,z_n) - v_s\ R = 0, \qquad s = 1,\ldots,n \tag{21a}$$

$$1 - \sum_j z_j = 0, \qquad j = 1,\ldots,n \tag{21b}$$

where

$$w_s(z_1,\ldots,z_n) = f_s z^{\alpha^s} - r_s z^{\beta^s}$$
$$z^{\alpha^s} = \prod_{j=1}^{n} z_j^{\alpha_{sj}}, \qquad z^{\beta^s} = \prod_{j=1}^{n} z_j^{\beta_{sj}}$$
$$\alpha^s = (\alpha_{s1},\ldots,\alpha_{sn}), \qquad \beta^s = (\beta_{s1},\ldots,\beta_{sn})$$

We are assuming that

1. The rank of stoichiometric matrix
$$rk\Gamma = n - 1 \tag{22}$$
It follows from Equation (19) that in this case we have a single reaction route, i.e. $P = 1$.
We are also assuming that[8]
2. $$\|\alpha^s\| = \sum_j \alpha_{sj} = \|\beta^s\| = p_s, \qquad \alpha^s \neq \beta^s \tag{23}$$
Finally, we assume that
3. $R = 0$ is not a generic root of system (21).

Horiutis numbers $v_1,\ldots,v_n$ have the following property

$$\sum_s v_s(\beta^s - \alpha^s) = 0 \tag{24}$$

---

[8] We consider the systems in which each intermediate contains the same number of active sites, e.g. AZ, BZ (Z is the catalytic site) or PtO, PtCO include only one catalyst site. This assumption simplifies the analysis. However, our results can be generalized to systems, in which surface intermediate include more that one active site or the catalyst surface is characterized by more than one type of active sites.

Up to the scaling, they are co-factors Δ_s of elements of any column of stoichiometric matrix Γ (see, for instance, Bykov et al., 1998; Lazman and Yablonskii, 1991).[9] We can always assign the directions of elementary reactions so that all stoichiometric coefficients are non-negative and this will be assumed later.

At these assumptions, system (21) has the resultant with respect to reaction rate R (Bykov et al., 1998; Lazman and Yablonskii, 1991). This means that there exists the polynomial

$$\mathrm{Res}(R) = B_L R^L + \ldots + B_1 R + B_0 \tag{25}$$

vanishing if R is the root of system (21). Vanishing of the resultant is the necessary (and in some cases sufficient) condition of algebraic system solvability (see Gel'fand et al., 1994; van der Waerden, 1971).

The right-hand side of Equation (25) is the kinetic polynomial. Assuming $v_1 \neq 0$, we can define the resultant with respect to R as

$$\mathrm{Res}(R) = \prod_j \left(f_1 z_{(j)}^{\alpha^1} - r_1 z_{(j)}^{\beta^1} - v_1 R\right) \tag{26}$$

where $z_{(j)}$ are the roots of the system

$$w_s(z_1, \ldots, z_n) - v_s \; R = 0, \qquad s = 1, \ldots, n, \;\; s \neq k \tag{27a}$$

$$1 - \sum_j z_j = 0, \qquad j = 1, \ldots, n \tag{27b}$$

at fixed R and $k = 1$ (see Bykov et al., 1987, 1998; Lazman and Yablonskii, 1991 for a background and rigorous proof).

In our assumptions, system (27) has the finite number of roots (by Lemma 14.2 in Bykov et al., 1998), so that the product in Equation (26) is well defined. We can interpret formula (26) as a corollary of Poisson formula for the classic resultant of homogeneous system of forms (i.e. the *Macaulay* (or *Classic*) *resultant*, see Gel'fand et al., 1994). Moreover, the product Res(R) in Equation (26) is a polynomial of R-variable and it is a rational function of kinetic parameters f_s and r_s (see a book by Bykov et al., 1998, Chapter 14). It is the same as the classic resultant (which is an irreducible polynomial (Macaulay, 1916; van der Waerden, 1971) up to constant in R multiplier.[10] In many cases, finding resultant allows to solve the system (21) for all variables.[11]

---

[9] Note, that property (22) guarantees that for some i we have non-zero v_i.

[10] It is possible to prove that our system (21) has a *sparse* (or *toric*) resultant in sense of Gel'fand et al. (1994). Non-trivial moment here is the importance of the stoichiometric condition (24).

[11] Certain properties of the resultant derivatives by parameters allow finding all the coordinates of the solution (see a book by Gel'fand et al., 1994).

2.2.2 The cyclic characteristic and the thermodynamic consistency

At the thermodynamic equilibrium, all steps of the detailed mechanism should be to be at the equilibrium, i.e.

$$w_s(\mathbf{z}) = 0, \qquad s = 1, \ldots, n \tag{28}$$

Thus, we have $R = 0$ at the equilibrium. Equation (28) together with the linear balance Equation (27b) form an overdetermined system of $z_1, \ldots z_n$. As we assume that $R = 0$ is not a generic root of the system, the only possibility for system (27b)+(28) to have a solution is satisfying certain constraints on kinetic parameters. We can rewrite Equation (28) as

$$f_s z^{\alpha^s} = r_s z^{\beta^s}, \qquad s = 1, \ldots, n \tag{29}$$

After raising both sides of equation to the power of ν_s, multiplying transformed equations and applying condition (24), we conclude that the necessary condition for system (27b)+(28) to have a solution with non-zero coordinates[12] is

$$\prod_{s=1}^{n} (f_s/r_s)^{\nu_s} = 1 \tag{30}$$

Equilibrium constraint (30) can be expressed as

$$K_{\text{eq}} = \frac{f^-(\overleftarrow{c})}{f^+(\vec{c})} \tag{31}$$

where

$$K_{\text{eq}} = \prod_{s=1}^{n} (k_s/k_{-s})^{\nu_s} \tag{32}$$

is the equilibrium constant of the net reaction (k_s and k_{-s} are kinetic constants), $f^-(\overleftarrow{c})$ the product of concentrations of the net reaction products and $f^+(\vec{c})$ the product of concentrations of the net reaction reactants, respectively. Naturally, condition (31) has exactly the same form as the equilibrium condition for the linear reaction mechanism (see Equation (8)). Both conditions (8) and (31) correspond to the MAL for the net reaction. The only difference is that for non-linear mechanism, ν_s in Equation (32) can be different from values 1 (and 0) in corresponding formulas for the linear mechanism (compare with Equations (1b) and (1c)).

It is intuitively clear that the structure of resultant (25) should reflect the equilibrium constraint (30). Let us call the binomial

$$C = \prod_{s=1}^{n} f_s^{\nu_s} - \prod_{s=1}^{n} r_s^{\nu_s} \tag{33}$$

the *cyclic characteristic*. Since $R = 0$ is not (generic) zero of system (21), the constant term B_0 of kinetic polynomial is not identically zero. We have proved

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[12] Owing to assumption #3, system (27b)+(28) cannot have the solution with zero z_s for generic values of reaction weights.

(Bykov et al., 1998; Lazman and Yablonskii, 1991; Lazman et al., 1985a) that the constant term B_0 in Equation (25) is the non-zero multiple of the cyclic characteristic (33).

More precisely, the following proposition is valid (see Theorem 14.1 in a monograph by Bykov et al., 1998). We are assuming that none of rational fractions $B_0,\ldots,B_L$ in Equation (25) is reducible. We write $B_0 \sim B$ if $B_0/B \neq 0$ for generic $f_1, r_1, \ldots, f_s,\ r_s \neq 0$.

Proposition 1. In the assumptions of the Basic Case

$$B_0 \sim C^p \tag{34}$$

The Horiuti numbers defining the cyclic characteristic in Equation (34) are relatively prime i.e. $\mathrm{GCD}(v_1, \ldots, v_n) = 1$. The exponent p in Equation (34) is the natural number. If we assume additionally that

$$v_s \neq 0, \qquad s = 1, \ldots, n \tag{35}$$

then,

$$p = \mathrm{GCD}(\Delta_1, \ldots, \Delta_n) \tag{36}$$

(see[13] Corollary 14.1 in the monograph by Bykov et al., 1998). Property (34) ensures the thermodynamic consistence of kinetic polynomial: if $R = 0$, the cyclic characteristic (33) should vanish.[14]

Cyclic characteristic has following property (see Bykov et al., 1998, Corollary 14.2).

Proposition 2. If $p > 1$ and property (35) is valid, then the cyclic characteristic C is contained in the coefficients B_s of kinetic polynomial (25) with an exponent equal at least to $p - s,\ \ s = 0, 1, \ldots, p-1$, but it is not contained in the leading coefficient $\mathrm{B_L}$.

This means that we could have a situation when more than one root of kinetic polynomial vanishes at the thermodynamic equilibrium. However, only one of these roots would be feasible.

2.2.3 Coefficients of the kinetic polynomial

For sufficiently small $|R|$ the following formula is valid (Bykov et al., 1998; Lazman and Yablonskii, 1991)

$$\frac{d \ln \mathrm{Res}(R)}{dR} = -\sum_{k=1}^{n} v_k \sum_{j_k=1}^{M_k} 1/(w_k(\mathbf{z}_{j_k}(R)) - v_k R) \tag{37}$$

---

[13] GCD in Equation (36) is the *Greatest Common Divisor*, i.e. the largest positive integer that divides integer numbers in ().

[14] We have found recently the topological interpretation of property (34). The stoichiometric constraints (24) can be interpreted in terms of the topological object, the *circuit*. Existence of the circuit "explains" the appearance of the cyclic characteristic in the constant term of kinetic polynomial. Thus, we can say that in some sense the correspondence between the detailed mechanism and thermodynamics is governed by pure topology.

where $\mathbf{z}_{j_k}(R)$ is zero of the system (27). The latter has a finite number of zeros in the assumptions of the *Basic case* (see Bykov et al., 1998; Lazman and Yablonskii, 1991). Let

$$d_k = \frac{d^k \ln \mathrm{Res}(R)}{dR^k}\bigg|_{R=0} \tag{38}$$

Then,

$$B_k = \left(\frac{1}{k!}\right)\sum_{j=1}^{k} B_{k-j}d_j/(j-1)!, \qquad k = 1,\ldots,L \tag{39}$$

It follows from Equations (37)–(39) that the coefficients of the kinetic polynomial are symmetric functions of zeroes of systems (27) for $k = 1, \ldots, n$ at $R = 0$, i.e. *equilibrium subsystems.*

Formula for the first coefficient of the kinetic polynomial is

$$\frac{B_1}{B_0} = -\sum_{k=1}^{n} \nu_k \sum_{j_k=1}^{M_k} 1/w_k(\mathbf{z}_{j_k}(0)) \tag{40}$$

The symbolic algorithm based on multi-dimensional residues theory their implementation is described in Bykov et al., 1998.[15]

2.2.4 Kinetic polynomial as the generalized overall reaction rate equation

2.2.4.1 The root count. (*The reader interested first in deriving explicit reaction rate equation may omit this section and start to read Section 2.2.4.2*)

Vanishing of the resultant Res(R) is a necessary and sufficient condition for R to be the coordinate of the zero of system (21). Thus, equation

$$\mathrm{Res}(R) = 0 \tag{41}$$

defines the overall reaction rate calculated in the assumptions of QSSA. The Res(R) is a polynomial of degree L in R. Generally, we have

$$L \le N \tag{42}$$

where N is the number of all isolated zeros (i.e. such $z_1, \ldots, z_n,\ W \in C^{n+1}$ that solve system (21)). It is important to have estimates for number of roots in various domains.

2.2.4.1.1 Bezout root count. Let

$$p_s = \max\left(\left\|\alpha^s\right\|, \left\|\beta^s\right\|\right)$$

be the *reaction order* of stage sth stage. Let us call the reaction with index μ, such that $p_\mu = \min(p_1, \ldots, p_n)$ and $\nu_\mu \neq 0$, the *minor reaction.*

---

[15] Note that standard procedures, such as Groebner Bases, that are built into the modern computer algebra systems (e.g. Maple) cannot handle our systems efficiently (see monograph by Bykov et al., 1998).

Proposition.

$$N \leq L_\mu = \prod_{s \neq \mu}^{n} p_s \tag{43}$$

Proof. We can write the system (21) in the *reduced* form as

$$\begin{gathered} v_\mu w_i(\mathbf{z}) - v_i w_\mu(\mathbf{z}) = 0, \qquad i \neq \mu \\ 1 - \sum_i z_i = 0 \\ R - \frac{1}{v_\mu} w_\mu(\mathbf{z}) = 0 \end{gathered} \tag{44}$$

Then the estimate (43) follows from the classic Bezout theorem (see van der Waerden, 1971) applied to the system (44). Estimate (43) shows that overall number of zeroes of system (21) does not exceed the product of reactions order of all reactions except the minor one.[16]

2.2.4.1.2 *Number of interior roots.* System (21) may have both *interior* ($z_i \neq 0$, $i = 1, \ldots, n$) and *boundary* roots ($\exists i \colon z_i = 0$). As a rule, boundary roots correspond to the zero reaction rate. Some classes of mechanisms can be free of boundary roots at all. For instance, system (21) corresponding to the mechanism of the *Basic case* type, satisfying the condition (35) does not have boundary roots. All interior roots belong to the algebraic tore. Bernstain theorem (see Gel'fand et al., 1994) can be applied to estimate the number of roots in this case.

2.2.4.1.3 *Number of feasible roots.* Usually we are interested mostly in the feasible roots of the system (21). The feasible roots of system (21) are real roots satisfying constraints

$$z_i \geq 0 \tag{45}$$

Thus, for system (21) the feasible domain is $S_n \times \mathcal{R}$ where S_n is n-dimensional standard simplex. Generally, the number of feasible roots depends on the parameters of system (21) (i.e. the reaction weights). The domains in the space of parameters with different number of feasible roots are the semi-algebraic sets (i.e. the sets, corresponding to some system of polynomial equations and inequalities). Analysis of the semi-algebraic domains is a difficult problem in computer algebra (see a monograph by Bykov et al., 1998). Asymptotic analysis (the *critical simplification*) allows obtaining the simple description of the domains of multiplicity for important mechanisms (Yablonsky et al., 2003).

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[16] Estimate (43) could be generalized to the multi-route mechanism — we can drop at least P reactions from Bezout root count.

2.2.4.2 Kinetic polynomial for model mechanisms

2.2.4.2.1 Eley–Rideal mechanism. Kinetic polynomial corresponding to the mechanism

$$\begin{array}{lll} (1) & A_2 + 2Z \Leftrightarrow 2AZ & [1] \\ (2) & AZ + B \Leftrightarrow AB + Z & [2] \end{array} \tag{46}$$

of heterogeneous catalytic reaction

$$A_2 + 2B \Leftrightarrow 2AB \tag{47}$$

is

$$4(f_1 - r_1)R^2 - (4r_1r_2 + 4f_1f_2 + (f_2 + r_2)^2)R + f_1f_2^2 - r_1r_2^2 = 0 \tag{48}$$

where $f_1 = k_1c_{A_2}$, $r_1 = k_{-1}$, $f_2 = k_2c_B$, and $r_2 = k_{-2}c_{AB}$. Here k_1, k_{-1}, k_2 and k_{-2} are reaction constants of corresponding elementary reactions of mechanism (46) and c_{A_2}, c_B and c_{AB} are concentrations of corresponding reactants and products. Note that coefficients of the kinetic polynomial (48) are polynomials in reaction weights (sometimes named reaction frequencies) f_1, r_1, f_2 and r_2.[17] Obviously, these coefficients are *not* constants: they depend on reaction weights that, in turn, depend on temperature and concentrations of reactants and products of the net reaction. Thus, coefficients of kinetic polynomial are functions of temperature and concentrations of net reaction reagents.

If we add up the chemical equations of mechanism (46) multiplied by corresponding stoichiometric numbers (i.e. 1 and 2), we obtain the equation of net reaction (47). Note how the constant term of Equation (48) and exponents in its terms correspond to the Proposition 1 (and property (36)). The only feasible root of polynomial (48) is

$$R = \frac{2(f_1f_2^2 - r_1r_2^2)}{4r_1r_2 + 4f_1f_2 + (f_2 + r_2)^2 + (f_2 + r_2)\sqrt{(f_2 + r_2)^2 + 8(f_1f_2 + r_1r_2) + 16f_1r_1}} \tag{49}$$

2.2.4.2.2 Langmuir–Hinshelwood mechanism. More interesting is the kinetic polynomial corresponding to the mechanism

$$\begin{array}{lll} (1) & A_2 + 2Z \Leftrightarrow 2AZ & [1] \\ (2) & B + Z \Leftrightarrow BZ & [2] \\ (3) & AZ + BZ \Leftrightarrow AB + 2Z & [3] \end{array} \tag{50}$$

of reaction (47). This mechanism is the standard "building block" of the models describing the critical phenomena in heterogeneous catalytic reactions (for instance, CO oxidation) (Bykov and Yablonskii, 1977a, b; Yablonskii and Lazman, 1996). Kinetic polynomial corresponding to the mechanism (50) is

$$B_4R^4 + B_3R^3 + B_2R^2 + B_1R + B_0 = 0 \tag{51}$$

---

[17] f_i are *reaction weights* (or *reaction frequencies*) of forward reactions and r_i reaction weights of reverse reactions.

where

$$B_0 := -r_2^2 r_1 (f_1 f_2^2 f_3^2 - r_2^2 r_3^2 r_1)$$

$$\begin{aligned}B_1 := {} & 8r_2^3 r_3^2 r_1^2 + 2r_2^4 r_1 r_3^2 + 4r_2^4 r_1^2 r_3 + f_2^2 r_2^2 f_3^2 r_1 + 2f_2^2 r_2^2 f_3 r_3 r_1 \\ & + 4f_2^2 r_2^2 r_1^2 r_3 + f_2^4 f_3^2 r_1 + 2f_2 r_2^3 f_3 r_3 r_1 + 8f_2 r_2^3 r_1^2 r_3 + 2f_2^3 r_2 f_3^2 r_1 \\ & - f_1 f_2^2 r_2^2 f_3^2 + 8f_1 f_2^2 r_2^2 r_1 f_3 + 4f_1 r_2^3 f_3 r_3 r_1 + 4f_1 r_2^4 r_3 r_1 - 4f_1 f_2^2 r_2 f_3^2 r_1 \\ & + 8f_1 f_2 r_2^3 f_3 r_1 + 4f_1 f_2 r_2^2 f_3^2 r_1\end{aligned}$$

$$\begin{aligned}B_2 := {} & -4r_2^4 r_3 r_1 + 4f_1^2 r_2^2 f_3^2 + 24f_2^2 r_2^2 r_1^2 + 8f_1^2 f_3 r_2^3 - 4f_2^4 r_1 f_3 - 8f_1 r_2^4 r_1 \\ & + f_2^4 f_3^2 + 16f_2^3 r_2 r_1^2 + 16r_2^3 r_1^2 r_3 + f_2^2 r_2^2 f_3^2 + 16f_2 r_2^3 r_1^2 + 4f_1 r_2^4 r_3 \\ & - 4f_2^3 f_3^2 r_1 + 8r_2^3 r_1 r_3^2 + 2f_2^3 r_2 f_3^2 + 24r_2^2 r_3^2 r_1^2 + 4f_1^2 r_2^4 + 4r_2^4 r_1^2 + r_2^4 r_3^2 \\ & + 4f_2^4 r_1^2 - 16f_1 f_2 r_2^3 r_1 + 4f_1 f_2^2 r_2^2 f_3 - 4f_1 f_2^2 r_2 f_3^2 - 4f_1 f_2^2 f_3^2 r_1 \\ & + 4f_1 f_2 f_3 r_2^3 + 4f_1 r_2^3 f_3 r_3 - 8f_1 r_2^3 r_1 f_3 + 16f_1 r_2^3 r_3 r_1 - 4f_1 r_2^2 f_3^2 r_1 \\ & + 2f_2 r_2^3 f_3 r_3 - 4f_2 r_2^3 r_1 f_3 - 8f_2 r_2^3 r_3 r_1 + 32f_2 r_2^2 r_1^2 r_3 - 8f_1 f_2^2 r_2^2 r_1 \\ & + 2f_2^2 r_2^2 f_3 r_3 - 12f_2^2 r_2^2 r_1 f_3 - 4f_2 r_2^2 f_3^2 r_1 - 8f_2^2 r_2 f_3^2 r_1 + 16f_2^2 r_2 r_1^2 r_3 \\ & - 4f_2^2 r_2^2 r_3 r_1 - 8r_2^3 f_3 r_3 r_1 - 12f_2^3 r_2 r_1 f_3 - 8f_2 r_2^2 f_3 r_3 r_1 + 16f_1 f_2 r_2^2 r_1 f_3 \\ & + 24f_1 r_2^2 f_3 r_3 r_1 + 24f_1 f_2^2 r_2 r_1 f_3 + 16f_1 f_2 r_2 f_3^2 r_1\end{aligned}$$

$$\begin{aligned}B_3 := {} & 16f_1^2 r_2^2 f_3 + 16f_1^2 f_3^2 r_2 - 4f_1 r_2^2 f_3^2 - 8f_1 f_2^2 f_3^2 + 32r_3^2 r_1^2 r_2 + 8r_2^2 r_3^2 r_1 \\ & + 16r_2^2 r_3 r_1^2 + 4r_2^2 r_1 f_3^2 - 16r_2^2 r_3 r_1 f_3 + 16f_2^2 r_3 r_1^2 + 4f_2^2 r_1 f_3^2 + 8f_2 r_2 r_1 f_3^2 \\ & - 24f_2 r_2 r_3 r_1 f_3 + 32f_2 r_2 r_3 r_1^2 - 8f_2^2 r_3 r_1 f_3 + 48f_1 r_2 r_3 r_1 f_3 + 16f_1 r_2^2 r_3 r_1 \\ & - 16f_1 r_2 r_1 f_3^2 - 16f_1 r_2^2 r_1 f_3 + 8f_1 r_2^2 f_3 r_3 + 16f_1 f_2^2 r_1 f_3 + 16f_1 f_2 r_1 f_3^2 \\ & - 8f_1 f_2 f_3^2 r_2\end{aligned}$$

$$B_4 := 16f_1^2 f_3^2 - 16f_1 r_1 f_3^2 + 16r_3^2 r_1^2 + 32f_1 r_3 r_1 f_3$$

here $f_1 = k_1 c_{A_2}$, $r_1 = k_{-1}$, $f_2 = k_2 c_B$, $r_2 = k_{-2}$, $f_3 = k_3$, and $r_3 = k_{-3} c_{AB}$. The 4th degree polynomial in R on the left-hand side of Equation (51) may have 1 or 3 feasible roots. Figure 1 shows the dependence of all four roots of this polynomial on the parameter f_2.[18] We can interpret the overall reaction rate R as a multi-valued algebraic function of f_2. Only one branch (denoted as R1) of this function passes through the point of thermodynamic equilibrium (see Figure 2). Far from equilibrium, however, this branch disappears in the bifurcation point where the branch R1 merges with the branch R2. Beyond the bifurcation point both branches become infeasible. They correspond to the pair of complex conjugated roots. Similar metamorphosis happens to the branches R2 and R3; the branch R4

[18] Up to scale, this is the dependence of overall reaction rate on concentration C_B in the assumption of constant temperature and concentrations c_{A_2} and C_{AB}. All figures in this chapter illustrate certain qualitative features of kinetic behavior, i.e. rate-limitation, vicinity of equilibrium, steady-state multiplicity, etc. Parameter values are selected to illustrate these qualitative features. Certainly these features could be illustrated with "realistic" kinetic parameters.

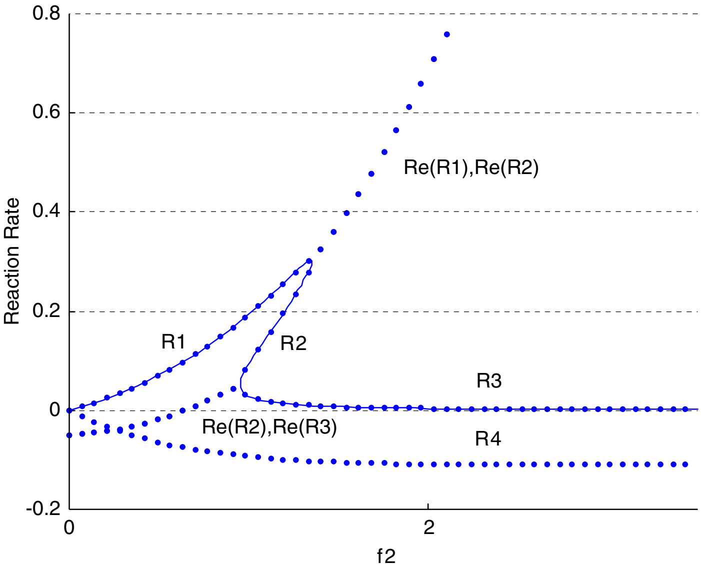

Figure 1 Dependence of overall reaction rate on the parameter f_2 (LH mechanism). Branches R1, R2, R3 and R4 represent the roots of kinetic polynomial. Solid line indicates feasible steady states. Branches Re(R1), Re(R2) and Re(R3) correspond to the real parts of conjugated complex roots of kinetic polynomial. Parameter values: $f_1 = 1.4$, $r_1 = 0.1$, $r_2 = 0.1$, $f_3 = 15$ and $r_3 = 2$.

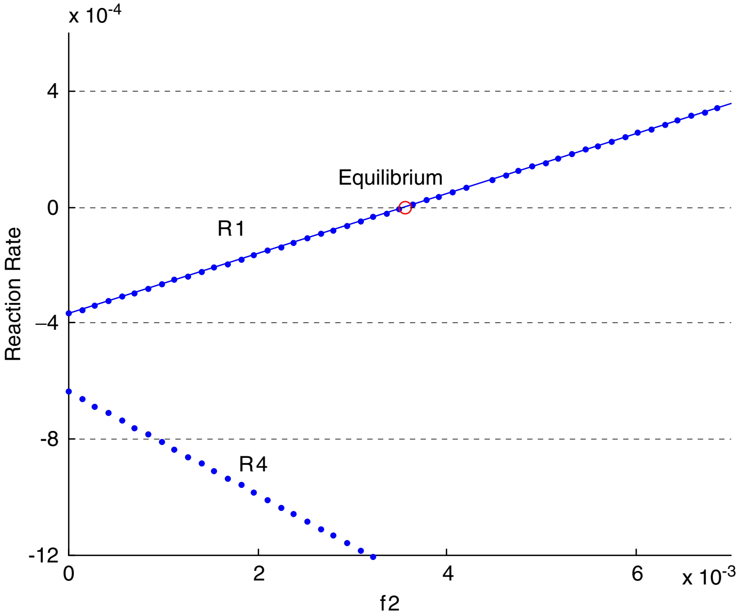

Figure 2 Overall reaction rate dependence (see Figure 1) in the vicinity of thermodynamic equilibrium.

is always infeasible. All these branches can be described implicitly by the single equation (51) in single variable R as the roots of *kinetic polynomial.*

3. REACTION RATE APPROXIMATIONS

Although it is possible to solve in radicals the 4th order polynomial corresponding to the LH mode, we will not even try to reproduce corresponding equations due to their intractability. Higher order polynomials would present even more difficulties for analytic treatment. Although analytic expressions for roots of algebraic equations are still possible (in terms of theta-functions; Mumford, 1984) one can imagine that tractability issue becomes more and more difficult for higher degree polynomials.

We consider below the possibilities for simplification of overall reaction rate equations and introduce the main result of this chapter — *the hypergeometric series for reaction rate.*

3.1 Classic approximations

3.1.1 Rate-limiting step

Let our mechanism contains a reaction step with index k such that

$$f_k, r_k \ll f_i, r_i, \qquad i \neq k$$

This step is called the rate-limiting step. Reaction rate approximation can be found in the form of power series (by f_k or r_k) (see Lazman and Yablonskii, 1988, 1991).

The first term of this series is the rate of rate-limiting step calculated at the equilibrium of the rest of reactions. This first term approximation is widely applied in heterogeneous catalysis. We have derived the following explicit formula (in the assumptions of the *Basic case*; see Lazman and Yablonskii, 1988).

$$R = \frac{f_k}{\nu_k} \frac{\left(1 - \prod_{j=1}^{n} (1/\kappa_j)^{\nu_j/\nu_k}\right)}{\left(\sum_{i=1}^{n} \prod_{j \neq k} (1/\kappa_j)^{\Delta_{ji}^{k}/(p_k \Delta_k)}\right)^{p_k}} \tag{52}$$

where $\kappa_j = f_j/r_j$, $p_k = ||\alpha^k|| = ||\beta^k||$ is the reaction order of the step k, Δ_k are co-factors of the element of kth row of matrix — Γ and $\Delta_{ji}^{k}$are co-factors of elements with indices j,i of matrix,

$$\Gamma_k' = \begin{pmatrix} \alpha_{11} - \beta_{11} & . & . & . & \alpha_{1n} - \beta_{1n} \\ . & . & . & . & . \\ \alpha_{k1} & . & . & . & \alpha_{kn} \\ . & . & . & . & . \\ \alpha_{n1} - \beta_{n1} & . & . & . & \alpha_{nn} - \beta_{nn} \end{pmatrix}$$

where

$$\prod_{j=1}^{n}\left(\frac{1}{\kappa_j}\right)^{\nu_j}=\left(\frac{1}{K_{\mathrm{eq}}}\right)\frac{F(c_{\mathrm{pr}})}{F(c_{\mathrm{r}})}$$

K_{eq} is the equilibrium constant, $F(c_{\mathrm{pr}})$ and $F(c_{\mathrm{r}})$ are functions of concentrations of products and reactants, respectively, which relate to the net reaction.

Example: LH mechanism, second step is the rate-limiting one

We have $\Delta_2=\nu_2=2, p_2=1$,

$$\Gamma_2'=\begin{pmatrix}2 & -2 & 0\\ 1 & 0 & 0\\ -2 & 1 & 1\end{pmatrix},\quad \Delta_{11}^2=0,\qquad \Delta_{31}^2=0,\qquad \Delta_{12}^2=-1,$$

$$\Delta_{32}^2=0,\qquad \Delta_{13}^2=1,\qquad \Delta_{33}^2=2$$

Substituting to Equation (52), we obtain

$$R=\frac{r_2}{2}\,\frac{\sqrt{\kappa_1}\kappa_2\kappa_3-1}{1+\sqrt{\kappa_1}\kappa_3+\kappa_1\kappa_3}$$

3.1.2 Vicinity of thermodynamic equilibrium

The cyclic characteristic C is small in the vicinity of thermodynamic equilibrium. We can find the overall reaction rate approximation in the vicinity of equilibrium either directly from kinetic polynomial or by expanding the reaction rate in power series by the small parameter C. The explicit expression for the first term is presented by Lazman and Yablonskii (1988, 1991). It is written as follows:

$$R=\left.\frac{\prod_{j=1}^{n}\kappa_j^{\nu_j}-1}{\sum_{k=1}^{n}\nu_k^2 f_k^{-1}\left(\sum_{i=1}^{n}\prod_{j\neq k}^{n}(1/\kappa_j)^{\Delta_{ji}^k/(p_k\Delta_k)}\right)^{p_k}}\right|_{\mathrm{eq}}\tag{53}$$

where $\prod_{j=1}^{n}\kappa_j^{\nu_j}=K_{\mathrm{eq}}F(c_{\mathrm{r}})/F(c_{\mathrm{pr}})$, K_{eq} is the equilibrium constant, $F(c_{\mathrm{pr}})$ and $F(c_{\mathrm{r}})$ functions of concentrations of products and reactants, respectively, which relate to the net reaction.

Note that denominator of Equation (53) should be calculated at equilibrium conditions. Formula (53) corresponds to the assumption of linear relation between the reaction rate and affinity of each reaction step (see Lazman and Yablonskii (1988, 1991) for detailed discussion). We can write

Equation (53) as

$$R = \frac{\prod_{j=1}^{n} \kappa_j^{\nu_j} - 1}{\sum_{k=1}^{n} \nu_k^2 / w_k|_{\mathrm{eq}}} \tag{53a}$$

where $w_k|_{\mathrm{eq}}$ is the reaction rate of forward (or reverse) reaction calculated at equilibrium conditions. In this form, this formula was known (Nacamura, 1958), however it was not the explicit expression of overall reaction rate in terms of parameters of reaction mechanism presented in this chapter, see Equation (53).

This linear affinity approximation does not always correspond to the linear approximation of kinetic polynomial $R \approx -(B_0)/(B_1)$. This happens only when degree p of cyclic characteristic in Proposition 1 (see Equation (34)) is one.[19] If $p > 1$, linear approximation of the kinetic polynomial does not correspond to the linear affinity relation (53). Equation $B_0 + B_1 R + \cdots + B_p R^p \approx 0$ is correct approximation in this case (see Lazman and Yablonskii, 1991).

3.2 Overall reaction rate as a hypergeometric series

The goal of this chapter, generally, is to present an analytical expression of the reaction rate branch which goes through the equilibrium point (*"thermodynamical branch" of the overall reaction rate*) with no classical assumption discussed earlier, i.e. "vicinity of the equilibrium" and "limiting step". This result is a logical continuation of the previously developed theory of the kinetic polynomial: that is why we had to explain main results of this theory, which are still not widely known. Posing this problem, i.e. deriving such analytical expression, and moreover its solving became possible only on the basis of last achievements of the algebraic theory. Some next sections will be devoted to the explanation of contemporary theoretical situation and its applications to the problems of complex kinetics.

3.2.1 Roots of algebraic equations: The hypergeometric series

As well known, we cannot solve general algebraic equation (with complex coefficients)

$$a_n x^n + \cdots + a_1 x + a_0 = 0 \tag{54}$$

in terms of radicals if $n > 4$ (Abel-Ruffini theorem, Galois theory, see a book by van der Waerden, 1971). For a long time mathematicians tried to find an analytic (not necessarily algebraic) solution to Equation (54). The situation was more or less clear already in the 19th century. First successes were summarized in the Felix Klein's (1888) book. A root of the quintic equation has been presented by Klein in terms of elliptic modular functions. At the same time, Klein mentioned

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[19] In this case, we can derive (53) from linear approximation of kinetic polynomial (Lazman and Yablonskii, 1991). See also Appendix 3, (A3.11) for details.

that solution of his equations could also be reduced to the studying solutions of some differential equations in terms of *hypergeometric* functions.[20] Well known to mathematicians, these facts are relatively obscure outside pure mathematics (most probably, due to absence of "standard" modern texts). Moreover, certain aspects of the problem are belonging to the relatively hot topic even in modern mathematics. Our major sources of mathematical facts are relatively recent papers by Sturmfels (2000) and Passare and Tsikh (2004). We will use the Sturmfels' results as a source of our formulas and we will use the very recent Passare and Tsikh's paper as a source for convergence conditions.

Sturmfels (2000) presented the complete set of equation (54) solutions in terms of the A-hypergeometric functions introduced before by Gel'fand et al. (1994). These functions are associated with the *Newton polytope N* of the polynomial on the left-hand side of Equation (54). The latter is the convex hull of the set A of the exponents of all monomials considered as integer lattice points in the corresponding real vector space. In the case of polynomial in single variable, the set A is the configuration of n+1 points 0, 1, …, n on the affine line. The Newton polytope here is just the line segment [0,n]. There are 2^{n-1} distinct complete sets of solutions of Equation (54) in terms of A-hypergeometric series. Each of these solutions corresponds to the particular *triangulation* of the set A that in our case is simply some subdivision

$$[0, i_1], [i_1, i_2], \ldots, [i_s, n], \qquad i_1 < i_2 < \ldots < i_s, \qquad i_k \in Z^+$$

of the segment [0,n]. The finest subdivision divides A into n segments of unit length whereas the coarsest one is just a single segment [0,n]. Sturmfels (2000) presented the general formula for the series solutions of Equation (54) and proved that there is a domain in the space of parameters of equation (54) where all n series for n roots of equation converge. For the finest subdivision $[0,1],[1,2],\ldots,[n-1,n]$, these series solution are

$$X_j = -\left[\frac{a_{j-1}}{a_j}\right] + \left[\frac{a_{j-2}}{a_{j-1}}\right], \qquad j = 1, 2, \ldots, n \tag{55}$$

where $\left[\frac{a_{-1}}{a_0}\right] = 0$, and[21]

$$\left[\frac{a_{j-1}}{a_j}\right] = \sum_{i_0 \geq 0, \ldots [j-1],[j], \ldots i_n \geq 0} \frac{(-1)^{i_j}}{i_{j-1}+1} \begin{pmatrix} i_j \\ i_1 \ldots i_{j-1} i_{j+1} \ldots i_n \end{pmatrix} \frac{a_0^{i_0} a_1^{i_1} \ldots a_{j-2}^{i_{j-2}} a_{j-1}^{i_{j-1}+1} a_{j+1}^{i_{j+1}} \ldots a_n^{i_n}}{a_j^{i_j+1}} \tag{56}$$

where i_0, i_1, …, i_n are non-negative integers satisfying the relations

$$\begin{aligned} i_0 + i_1 + \cdots + i_{j-1} - i_j + i_{j+1} + \cdots + i_n = 0 \\ i_1 + 2i_2 + \cdots + (j-1)i_{j-1} - ji_j + (j+1)i_{j+1} + \cdots + ni_n = 0 \end{aligned} \tag{57}$$

Note that series (56) has integer coefficients.

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[20] Klein considered this approach too cumbersome. Note that hypergeometric functions were applied to problem (54) as early as in 18th century.

[21] Here and below [] indicates that the corresponding index is omitted (see Equation (56)).

Recently Passare and Tsikh (2004) provided the detailed description of the domains of convergence of multi-dimensional hypergeometric series representing the roots of algebraic equations. They have relied on results of Birkeland obtained in 1920s. Birkeland found the Taylor series solutions to algebraic equations of the type

$$b_0 + b_1 y + \cdots + y^p + \cdots + y^q + \cdots + b_{n-1} y^{n-1} + b_n y^n = 0 \tag{58}$$

where p and q are two integers satisfying $0 \le p < q \le n$.

We can always reduce the problem (54) to the *dehomogenized* problem (58). Let

$$\begin{aligned} b_i &= \lambda_0 \lambda_1^i a_i, \quad & i &= 0,\ldots,n \\ y &= x/\lambda_1, \quad & \lambda_0, \lambda_1 &= C\setminus\{0\} \end{aligned} \tag{59}$$

To satisfy Equation (54) we can set $\lambda_1 = (a_p/a_q)^{1/(q-p)}$ and $\lambda_0 = a_p^{-1}\lambda_1^{-p}$ just substitute expressions (59) into Equation (58). There are exactly $(q-p)$ possible choices for parameters λ_0 and λ_1. The following Birkeland formula expresses the $(q-p)$ zeroes of Equation (58) as the Taylor series by parameters $b_0,\ldots,[p],\ldots,[q],\ldots,b_n$

$$Y_i = \sum_{k\in N^{n-1}} \frac{\varepsilon_i^{-\left\langle \beta_q,k\right\rangle+1}}{(q-p)k!} \frac{\Gamma\left(\left(-\left\langle \beta_q,k\right\rangle+1\right)/(q-p)\right)}{\Gamma\left(1+\left(\left\langle \beta_p,k\right\rangle+1\right)/(q-p)\right)} b_0^{k_0} b_1^{k_1},\ldots,[p],\ldots,[q],\ldots,b_n^{k_n} \tag{60}$$

where ε_i is any of the radicals $(-1)^{1/(q-p)}$, $i = 1,\ldots,(q-p)$, $k! = k_0!k_1!,\ldots,[p],\ldots,[q],\ldots,k_n!$, vectors β_p and β_q are corresponding rows of $(n+1)\times(n-1)$ matrix $B_{pq} = (\beta_\mu^v)$ which column vectors β^v are defined as $(q-p)e_v + (v-q)e_p + (p-v)e_q, v \neq p,q$ and $e_0, \ldots, e_n$ are the standard basis vectors in $\mathcal{R}^{n+1}$.

Note that both Equations (56) and (60) result in the same series for the root of kinetic polynomial corresponding the "thermodynamic branch" (see Appendix 4 for the proof).

3.2.2 Examples

We have applied the computer algebra (Maple) to generate the partial sums corresponding to the "brackets" (55).

3.2.2.1 Eley–Rideal mechanism. Kinetic polynomial here is quadratic in R (see Equation (48)). There is only one feasible solution (49) here. The feasible branch should vanish at the thermodynamic equilibrium. Thus, the only candidate for the feasible branch expansion is $R = -[B_0/B_1]$ because the second branch expansion is $R' = -B_2/B_1 + [B_0/B_1]$ and it does not vanish at equilibrium. First terms of series for reaction rate generated by formula (55) at $j = 1$ are

$$\begin{aligned} R = & -16{,}796\frac{B_0^{11}B_2^{10}}{B_1^{21}} - \frac{4{,}862B_0^{10}B_2^9}{B_1^{19}} - \frac{1{,}430B_0^9B_2^8}{B_1^{17}} - \frac{429B_0^8B_2^7}{B_1^{15}} - \frac{132B_0^7B_2^6}{B_1^{13}} \\ & - \frac{42B_0^6B_2^5}{B_1^{11}} - \frac{14B_0^5B_2^4}{B_1^9} - \frac{5B_0^4B_2^3}{B_1^7} - \frac{2B_0^3B_2^2}{B_1^5} - \frac{B_0^2B_2}{B_1^3} - \frac{B_0}{B_1} \end{aligned} \tag{61}$$

Birkeland's formula (60) applied to the dehomogenized polynomial $(1+y+b_2y^2)$ gives the following series (see Passare and Tsikh, 2004).

$$y = -\sum_{k=0}^{\infty} \frac{(2k)!}{(k+1)!} \frac{b_2^k}{k!} \equiv \frac{-1+\sqrt{1-4b_2}}{2b_2} \tag{62}$$

In our case, $n = 2$, $p = 0$, $q = 1$ and relations (59) give

$$R = B_0/B_1y, \qquad b_2 = B_0B_2/B_1^2 \tag{63}$$

It is easy to test that Equations (62) and (63) results in series (61).

Figure 3 compares the exact solution (49) and its approximations obtained by truncating series (61) at first, second, etc. terms. It shows that the even first term $(-B_0/B_1)$ provides reasonable approximation in the finite neighborhood of equilibrium. Addition of higher order terms increases the domain of close approximation. This is not surprising because the condition of convergence of this series is $b_2<1/4$ i.e. series (61) converges if the root is real which is always the case (see Equation (49)) for feasible values of parameters.

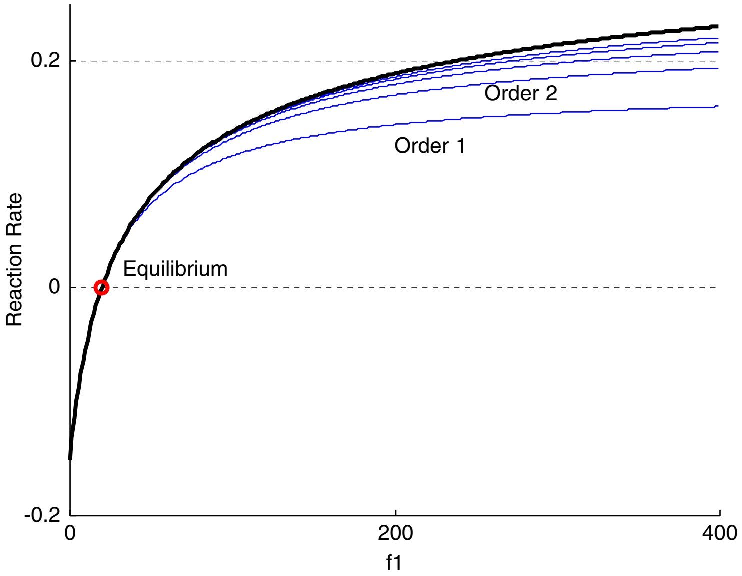

Figure 3 Overall reaction rate and its approximations by first 1, 2,..., 5 terms of hypergeometric series (Eley–Rideal mechanism). Parameters: $f_2 = 0.71$, $r_1 = 0.2$ and $r_2 = 7$.

3.2.2.2 Langmuir–Hinshelwood mechanism. Series expressions for roots of 4th order polynomial (51) are

$$\begin{aligned} X_1 &= -\left[\frac{B_0}{B_1}\right], \\ X_1 &= -\left[\frac{B_1}{B_2}\right] + \left[\frac{B_0}{B_1}\right], \\ X_2 &= -\left[\frac{B_2}{B_3}\right] + \left[\frac{B_1}{B_2}\right], \\ X_1 &= -\left[\frac{B_3}{B_4}\right] \end{aligned} \tag{64}$$

where[22]

$$\begin{aligned} \left[\frac{B_0}{B_1}\right] &= \frac{B_0}{B_1} + \frac{B_0^2 B_2}{B_1^3} - \frac{B_0^3 B_3}{B_1^4} + \frac{2B_0^3 B_2^2}{B_1^5} + \frac{B_0^4 B_4}{B_1^5} - \frac{5B_0^4 B_2 B_3}{B_1^6} + \cdots, \\ \left[\frac{B_1}{B_2}\right] &= \frac{B_1}{B_2} + \frac{B_1^2 B_3}{B_2^3} + \frac{2B_0 B_1 B_4}{B_2^3} - \frac{B_1^3 B_4}{B_2^4} - \frac{3B_0 B_1 B_3^2}{B_2^4} \\ &\quad + \frac{2B_1^3 B_3^2}{B_2^5} + \frac{12 B_0 B_1^2 B_3 B_4}{B_2^5} + \frac{6B_0^2 B_1 B_4^2}{B_2^5} + \cdots, \\ \left[\frac{B_2}{B_3}\right] &= \frac{B_2}{B_3} + \frac{B_2^2 B_4}{B_3^3} - \frac{3B_1 B_2 B_4^2}{B_3^4} + \frac{2B_2^3 B_4^2}{B_3^5} + \frac{4B_0 B_2 B_4^3}{B_3^5} + \cdots \\ \left[\frac{B_3}{B_4}\right] &= \frac{B_3}{B_4} \end{aligned} \tag{65}$$

Figures 4 and 5 compare the exact solutions of the kinetic polynomial (51) (i.e. the quasi-steady-state values of reaction rate) to their approximations. Even the first term of series (65) gives the satisfactory approximation of all four branches of the solution (see Figure 4). Figure 5, in which "brackets" from Appendix 2 are compared to the exact solution, illustrates the existence of the region (in this case, the interval of parameter f_2), where hypergeometric series converge for each root.

However, regions of convergence strongly depend on model parameters. Figures 6 and 7 illustrate this for the case of the steady-state multiplicity (parameters are the same as for Figure 1). Figure 7 shows that the approximation of feasible solution is satisfactory in the vicinity of the thermodynamic equilibrium. Intuitively, it is clear, because we can expect the convergence of our series for $\left[\frac{B_0}{B_1}\right]$ (see Equation (65)) at smaller values of B_0. Less obvious, it is an excellent approximation of the low-rate branch of the steady-state kinetic dependence *very far from thermodynamic equilibrium* (see Figure 6). For comparison, Figures 6 and 7 show the dependencies of the equilibrium approximation (53) as well as the approximation which corresponds to first

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[22] See Appendix 2 for more detailed "bracket" expressions.

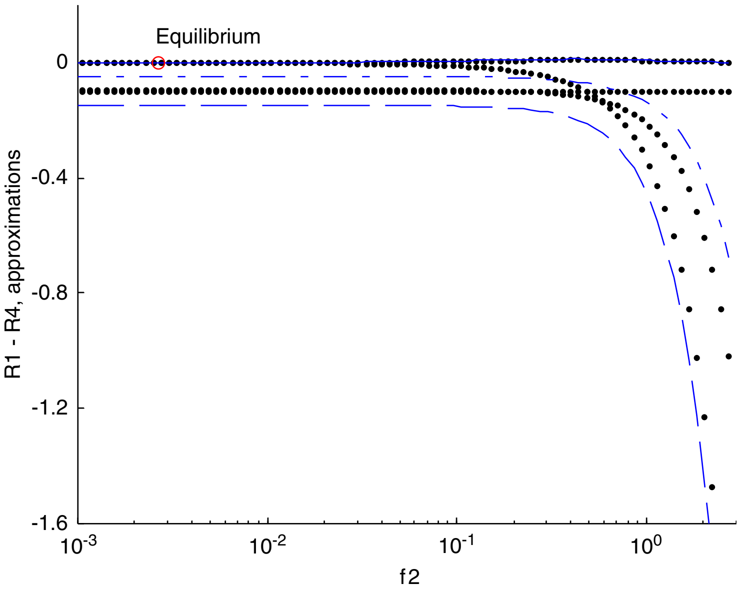

Figure 4 All roots of kinetic polynomial (dots) and their first-term (lines) approximations for LH mechanism. Parameters: $f_1 = 1.4$, $r_1 = 0.1$, $r_2 = 0.1$, $f_3 = 0.1$ and $r_3 = 0.01$.

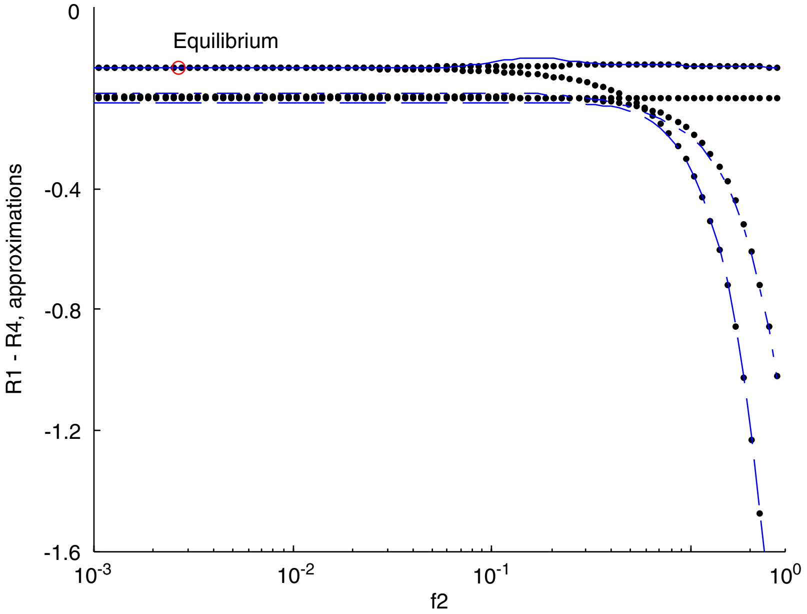

Figure 5 All roots of the kinetic polynomial from Figure 4 (dots) and their higher-order ($m = 3$) approximations (lines).

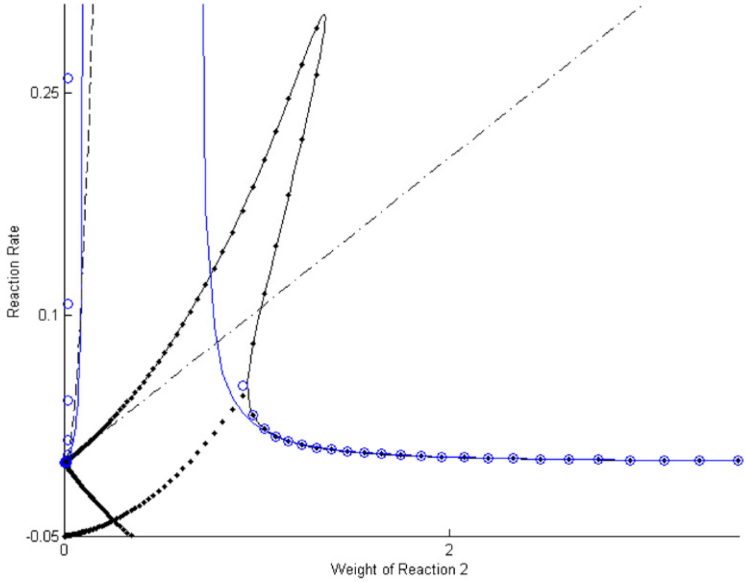

Figure 6 Approximations of the thermodynamic branch: steady-state multiplicity case (see Figure 1). Solid line is the first-term hypergeometric approximation. Circles correspond to the higher-order hypergeometric approximation ($m = 3$). Dashed line is the first-order approximation in the vicinity of thermodynamic equilibrium. Dash-dots correspond to the second-order approximation in the vicinity of thermodynamic equilibrium.

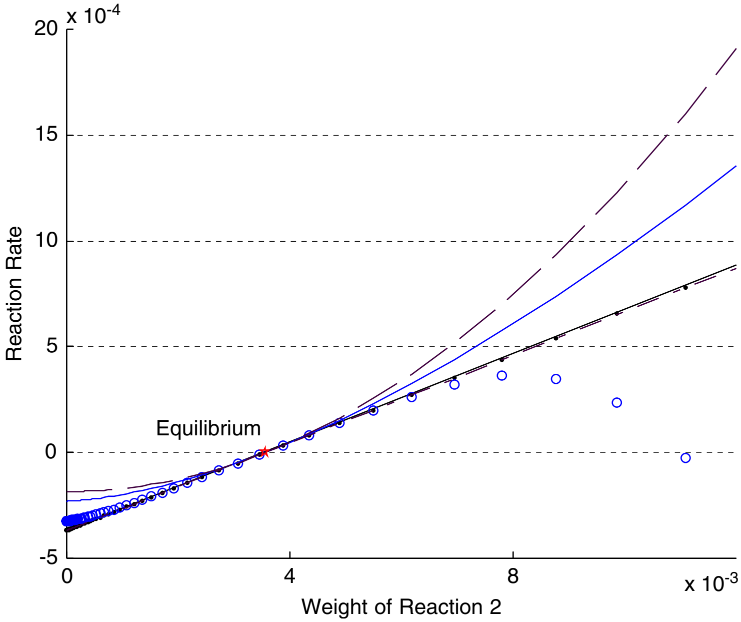

Figure 7 Approximations from Figure 6 in the vicinity of thermodynamic equilibrium.

terms of the expansion by parameter f_2 of feasible reaction rate branch in the vicinity of thermodynamic equilibrium. As expected, both formula (53) and expansion work in the vicinity of thermodynamic equilibrium. However, these approximations cannot predict the lower branch of reaction rate dependence. This example shows *the non-local nature* of hypergeometric series approximation.

At the same time, we see that practical application of this type of approximation requires the knowledge of the exact convergence conditions of these series. Surprisingly, the exact mathematical results here were obtained very recently (Passare and Tsikh, 2004) and the convergence theory still looks unfinished.

We are going to focus below on the series for the *thermodynamic branch*, i.e. the branch described by formula

$$R = -\left[\frac{B_0}{B_1}\right] \tag{66}$$

3.2.3 The thermodynamic branch

3.2.3.1 The conventional representation. We can write Equation (66) explicitly as follows

$$R = -\frac{B_0}{B_1} \cdot D \tag{67}$$

where

$$D = \sum_{i_2=0,\ldots,i_n=0}^{\infty} \frac{(-1)^{i_1}}{i_0+1} \binom{i_1}{i_2,\ldots,i_n} \cdot \frac{B_0^{i_0} \prod_{k=2}^{n} B_k^{i_k}}{B_1^{i_1}} \tag{68}$$

and

$$\begin{aligned} i_1 &= \sum_{k=2}^{n} k i_k, \\ i_0 &= \sum_{k=2}^{n} (k-1) i_k \end{aligned} \tag{69}$$

We know from Proposition 1 that the constant term $B_0 \sim C$ vanishes at the thermodynamic equilibrium. Some features of Equation (67) similar to the known LHHW-kinetic equation. There is a "potential term" B_0 responsible for thermodynamic equilibrium, there is a "denominator" B_1 of the polynomial type. However there is also a big difference. Equation (67) includes the term D, which is generated by the non-linear steps.

$$D = 1 + T_1 + T_2 + \cdots,$$

where T_i is the term of series (68). According to Propositions 1 and 2 each term T_i includes the multiplier C (i.e. the cyclic characteristic) in some integer degree d_i

$$T_i = t_i C^{d_i} \tag{70}$$

3.2.3.2 Validity of the thermodynamic branch. To show that series (67) actually represents the thermodynamic branch we have to prove that all terms of this series include the cyclic characteristic C in *positive* degree.

In the assumptions of the *Basic case*, this follows from the following facts

Proposition 3. If $p \geq 1$ and property (35) is valid, then the cyclic characteristic C is contained in the coefficient B_1 of kinetic polynomial with an exponent equal to $p-1$.

Proof. See Appendix 3.

Proposition 4. Degree d_i in Equation (70) is non-negative.

Proof. It follows from Propositions 1–3 and Equation (69) that in the case $p \leq 2$ we have

$$d_i \geq i_0 p - i_1(p-1) = \sum_{k=2}^{n} i_k(k-p) \geq 0$$

and in the case $p > 2$ we have

$$d_i \geq i_0 p - i_1(p-1) + \sum_{k=2}^{p-1} i_k(p-k) = \sum_{k=p}^{n} i_k(k-p) \geq 0$$

3.2.3.3 The four-term overall reaction rate equation. It follows from Propositions 1, 3 and the fact that the kinetic polynomial defined by formula (26) is a rational function of reaction weights f_s and r_s that we can write Equation (67) as

$$R = -\frac{B'_0}{B'_1} \cdot C(1 + t_1 C^{d_1} + \cdots + t_i C^{d_i} + \cdots) \tag{71}$$

where B'_0 and B'_1 are polynomials in f_s and r_s. Moreover, it follows from the theory (Bykov et al., 1998) that in the assumptions of the *Basic Case*, B'_0 is a monomial and we have proved in the Appendix 3 that B'_1 is not vanishing at the thermodynamic equilibrium. Note, that formula (1) for the linear mechanism is just a particular case of formula (71).

We can write (71) as a four-term overall reaction rate equation

$$R = \frac{k_+(f_+(c) - K_{\mathrm{eq}}^{-1} f_-(c))}{-B'_1} \left(1 + \sum_{i=1}^{\infty} t_i C^{d_i}\right) \tag{72}$$

where B'_1 is either coefficient B_1 or its multiplier, t_i $i = 1, 2, \ldots$ are rational functions in $k_{\pm i}$, c and integer degree d_i is non-negative. The latter property guarantees vanishing of reaction rate at the thermodynamic equilibrium. Equation (72) corresponds to Equation (14) with $M = 1$. In addition, similar to the HW equation, we have the kinetic term k_+, the potential term $f_+(c) - K_{\mathrm{eq}}^{-1} f_-(c)$ as well as the term $-B'_1$ which can be interpreted as the adsorption resistance term.

However, unlike the known approximations, our exact expression has the fourth term $(1 + \sum_{i=1}^{\infty} t_i C^{d_i})$ that represents the infinite series. Clearly, this term is generated by the non-linear steps. If all steps of the detailed mechanism are linear, such term is absent. It is important to understand the convergence of the series of fourth term.

3.2.4 The convergence domain

Detailed description of the domains of convergence of hypergeometric series in terms of *amoeba* of the *discriminant* of the polynomial has been given recently in Passare and Tsikh (2004). The discriminant $\Delta(a)$ is an irreducible polynomial with integer coefficients in terms of the coefficients a_i of polynomial (54) that vanishes if this polynomial has multiple roots. For instance, for cubic polynomial the discriminant is

$$\Delta(a) = 27a_0^2a_3^2 + 4a_1^3a_3 + 4a_0a_2^3 - 18a_0a_1a_2a_3 - a_1^2a_2^2 \tag{73}$$

The amoeba of a polynomial is the image of its zero locus under the mapping Log which relates each variable to the logarithm of its absolute value.

In the case of the quadratic equation, the convergence condition for the "thermodynamic branch" series is simply positive discriminant (Passare and Tsikh, 2004). For kinetic polynomial (48) this discriminant is always positive for feasible values of parameters (see Equation (49)). This explains the convergence pattern for this series, in which the addition of new terms extended the convergence domain.

For certain types of the series the explicit inequalities involving "mirror reflections" of the discriminant were possible (Passare and Tsikh, 2004). The situation is clearer for series depending on fewer variables. For instance, applying Birkeland approach, we can reduce to two the number of parameters in the case of cubic equation. The "thermodynamic branch" corresponds to the Birkeland series (60) for $p = 0$ and $q = 1$. The discriminant for cubic equation in Birkeland form is

$$\Delta(b_2, b_3) = 27b_3^2 + 4b_3 + 4b_2^3 - 18b_2b_3 - b_2^2 \tag{74}$$

The boundary of convergence domain is

$$\Delta(|b_2|, -|b_3|) = 0 \tag{75}$$

and the convergence domain is

$$27|b_3^2| - 4|b_3| + 4|b_2|^3 + 18|b_2||b_3| - |b_2|^2 < 0 \tag{76}$$

The following case study demonstrates the convergence behavior for the LH mechanism (50) with irreversible first stage (i.e. $r_{-1} = 0$). In this case the kinetic polynomial (51) always has (structurally unstable with respect to feasibility) zero root whereas three other roots could be found from the cubic equation

$$k_3R^3 + k_2R^2 + k_1R + k_0 = 0$$

where

$$k_3 := 16f_1^2f_3^2$$

$$\begin{aligned} k_2 :=\ & -8f_2^2f_1f_3^2 - 8f_2f_1f_3^2r_2 + 16f_1^2f_3r_2^2 + 8f_1f_3r_2^2r_3 \\ & -4f_1f_3^2r_2^2 + 16f_1^2f_3^2r_2 \end{aligned}$$

$$\begin{aligned} k_1 := & f_3^2f_2^4 + 2f_3^2r_2f_2^3 - 4f_1f_3^2r_2f_2^2 + r_2^2f_3^2f_2^2 + 2f_3f_2^2r_2^2r_3 \\ & + 4f_1f_3f_2^2r_2^2 + 2r_2^3f_3f_2r_3 + 4f_1r_2^3f_3f_2 + 8f_1^2f_3r_2^3 + 4f_1^2r_2^4 \\ & + 4f_1r_2^4r_3 + 4f_1f_3r_2^3r_3 + 4f_1^2f_3^2r_2^2 + r_2^4r_3^2 \end{aligned}$$

$$k_0 := -f_1f_3^2r_2^2f_2^2$$

Figure 8 shows the convergence domain (75) (i.e. the rhomboid) and coefficients $b_2 = (k_0k_2)/(k_1^2)$ and $b_3 = (k_0^2k_3)/(k_1^3)$ as parametric function of parameter $f_2 \in [0, \infty]$ at different values of f_3 (i.e. ovals). At lower values of parameter f_3 the whole loop is located within the convergence domain. This means that the series will converge for any $f_2 \in [0, \infty]$. At some value of f_3, the ovals start intersecting the rhomboid boundary. In this case we can have (at least) two convergence intervals $f_2 \in [0, f_2^*]$ and $f_2 \in [f_2^{**}, \infty]$ separated by interval $<s>$ of non-convergence.

Figure 9 shows the convergence domain as well as steady-state multiplicity domain on f_2, f_1 plane. We can see that steady-state multiplicity is not generally

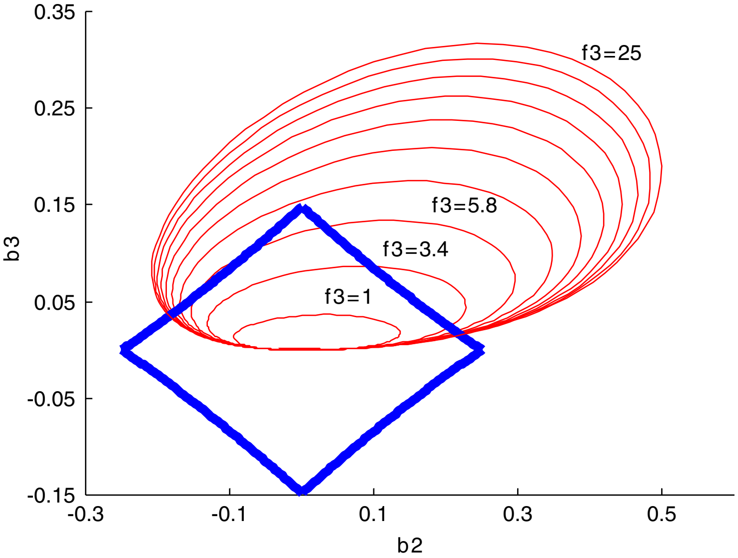

Figure 8 A convergence domain (rhomboid) and coefficients of the kinetic polynomial (ovals). The ovals represent the coefficients b2 and b3 as parametric functions of parameter f_2 at different values of parameter f_3. Parameters: $f_1 = 1.4$, $r_2 = 0.9$ and $r_3 = 0.4$.

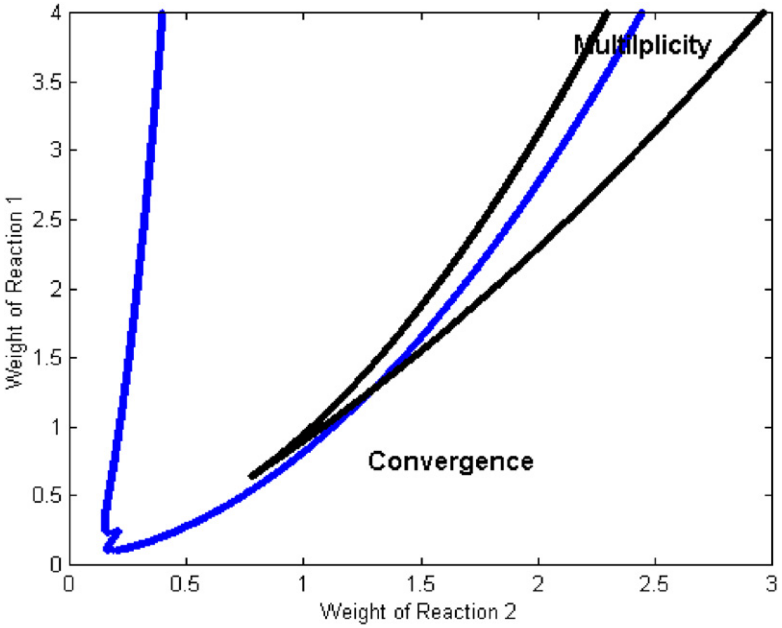

Figure 9 A convergence domain and steady-state multiplicity domain.

an obstacle to the convergence of hypergeometric series — one of the branches of the convergence domain boundary extends to the steady-state multiplicity region. Figure 9 shows also that convergence is lost before the bifurcation.

Figures 10–13 compare the exact dependencies of the (feasible) reaction rate and their first term approximation (i.e. $R = -(k_0)/(k_1)$) as well as approximation corresponding to $m = 3$:

$$\begin{aligned} R = & -10,010\frac{k_0^{10}k_2^3k_3^3}{k_1^{16}} - \frac{1,430k_0^9k_2^2k_3^3}{k_1^{14}} - \frac{165k_0^8k_2k_3^3}{k_1^{12}} - \frac{990k_0^8k_2^3k_3^2}{k_1^{13}} \\ & - \frac{12k_0^7k_3^3}{k_1^{10}} + \frac{180k_0^7k_2^2k_3^2}{k_1^{11}} + \frac{28k_0^6k_2k_3^2}{k_1^9} - \frac{84k_0^6k_2^3k_3}{k_1^{10}} + \frac{3k_0^5k_3^2}{k_1^7} \\ & - \frac{21k_0^5k_2^2k_3}{k_1^8} - \frac{5k_0^4k_2k_3}{k_1^6} + \frac{5k_0^4k_2^3}{k_1^7} - \frac{k_0^3k_3}{k_1^4} + \frac{2k_0^3k_2^2}{k_1^5} + \frac{k_0^2k_2}{k_1^3} + \frac{k_0}{k_1} \end{aligned}$$

Figure 9 shows that at smaller f_1 values the hypergeometric approximation works for the whole ray $f_2 \in [0, \infty]$ (see Figure 10).

At higher f_1 values we can have two convergence intervals (see Figure 11) or even 3 such intervals (see Figure 12, note that there is no significant difference between Figures 11 and 12, most probably due to the very small length of the middle interval). Finally, Figure 13 illustrates the convergence pattern in the region of steady-state multiplicity.

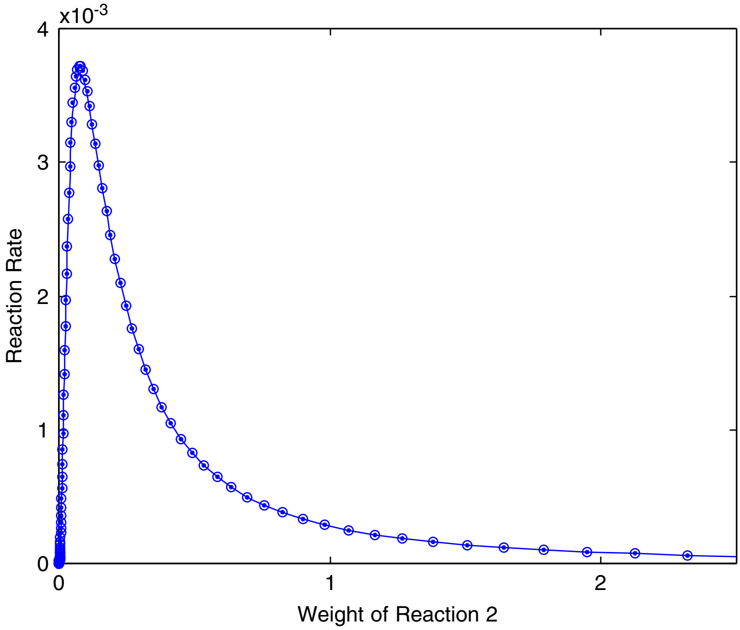

Figure 10 Exact overall reaction rate dependence (dots), its first-term hypergeometric approximation (solid line) and its higher-order ($m = 3$) hypergeometric approximation. Parameters: $f_1 = 0.01$, $r_2 = 0.2$, $r_3 = 1$ and $f_3 = 10$.

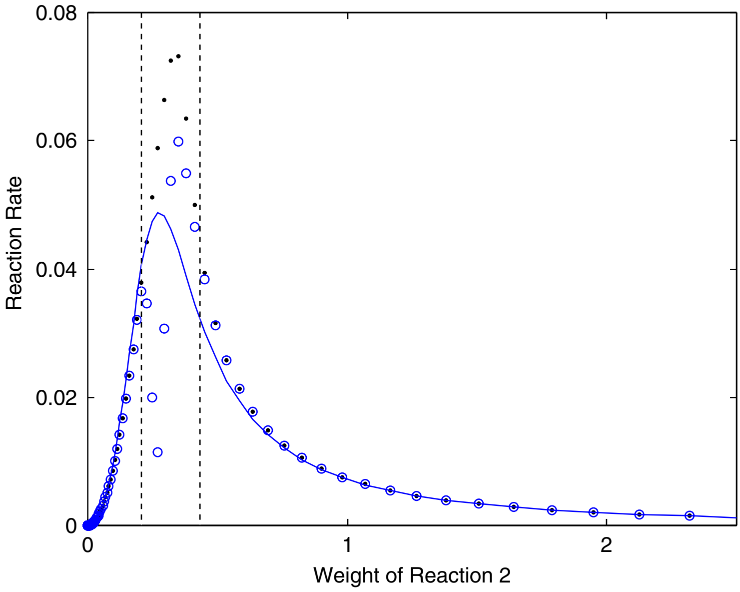

Figure 11 Dependencies from Figure 10 at $f_1 = 0.23$. Vertical dotted lines correspond to the boundaries of the convergence domain: there is no convergence in the interval between these boundaries.

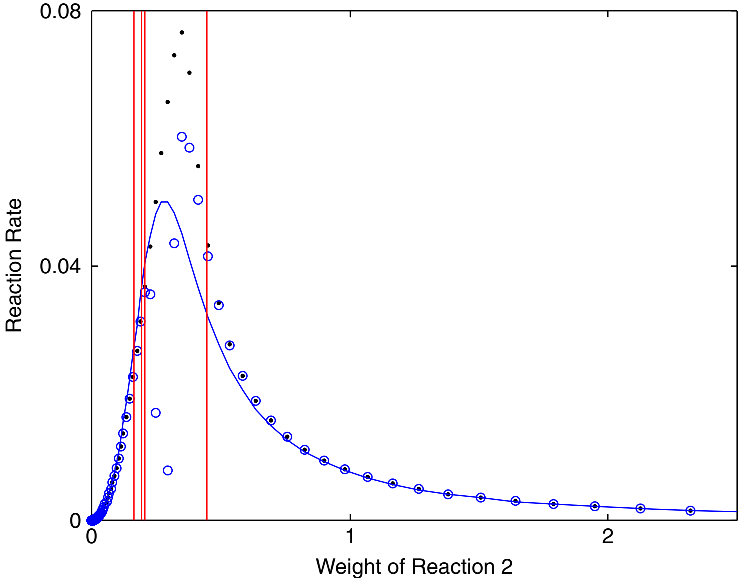

Figure 12 Dependencies from Figure 10 at $f_1 = 0.24$. There are four convergence boundaries in this case and three convergence domains (one of them is really narrow) separated by two non-convergence domains.

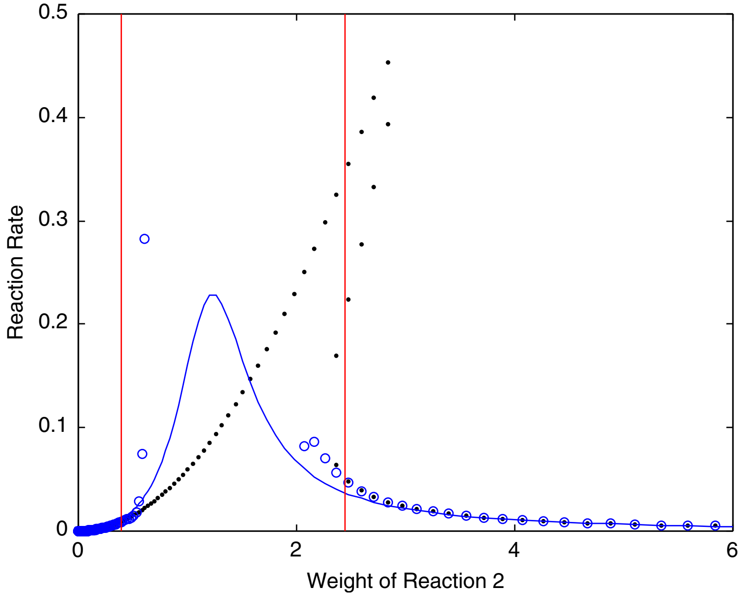

Figure 13 Dependencies from Figure 10 at $f_1 = 4$: case of the steady-state multiplicity.

3.2.5 Comparison to classic approximations

We are going to compare our hypergeometric approximation of the thermodynamic branch to the classic rate-limiting step and linear equilibrium approximations (see Sections 3.1.1 and 3.1.2).

We use the model corresponding to the LH mechanism as an example.

The case of step 1 limiting is shown in Figure 14. We can see that both classical and hypergeometric approximations fit well with the exact dependence in the vicinity of equilibrium as well as at lower values of parameter f_1. At the same time, we can see that hypergeometric approximation provides better fit at higher values of parameter f_1.

Figure 15 illustrates the case of step 2 limiting. Growth of the magnitude of kinetic parameters (in our case, 10-fold) unavoidably results in the degradation of the quality of rate-limiting type approximations (see Figure 15c). Whereas the equilibrium approximation works as expected in the vicinity of equilibrium, it does not produce good fit far from the equilibrium. The hypergeometric approximation produces uniformly good fit of the exact dependence (see Figure 15a–c).

Figure 16 demonstrates the similar features for the case of step 3 limiting.

Finally, Figure 17 compares all types of approximations and the exact reaction rate dependence. The equilibrium approximation works well at smaller values f_2 (the equilibrium point is close to the origin). Limitation of the step 1 works at higher values of parameter f_2 whereas limitation of step 2 fits the initial

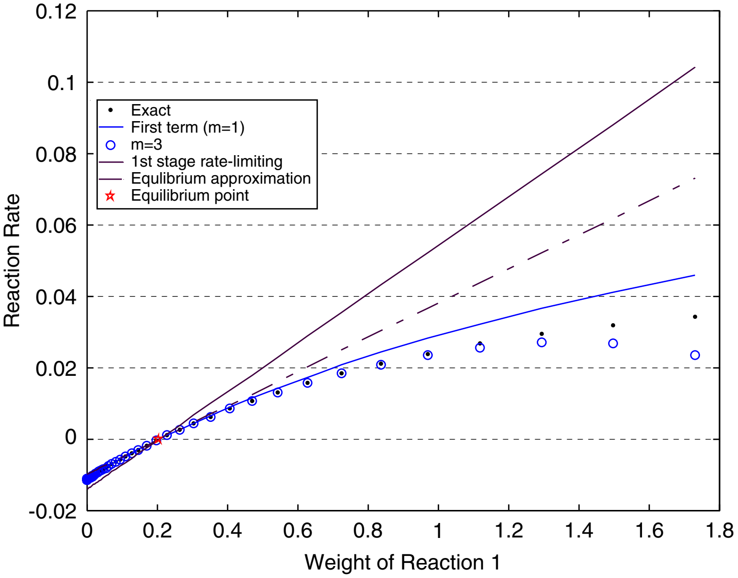

Figure 14 Overall reaction rate and its approximations: LH mechanism. Parameters: $r_1 = 0.1$, $f_2 = 14$, $r_2 = 10$, $f_3 = 1$ and $r_3 = 2$ (see Plate 1 in Color Plate Section at the end of this book).

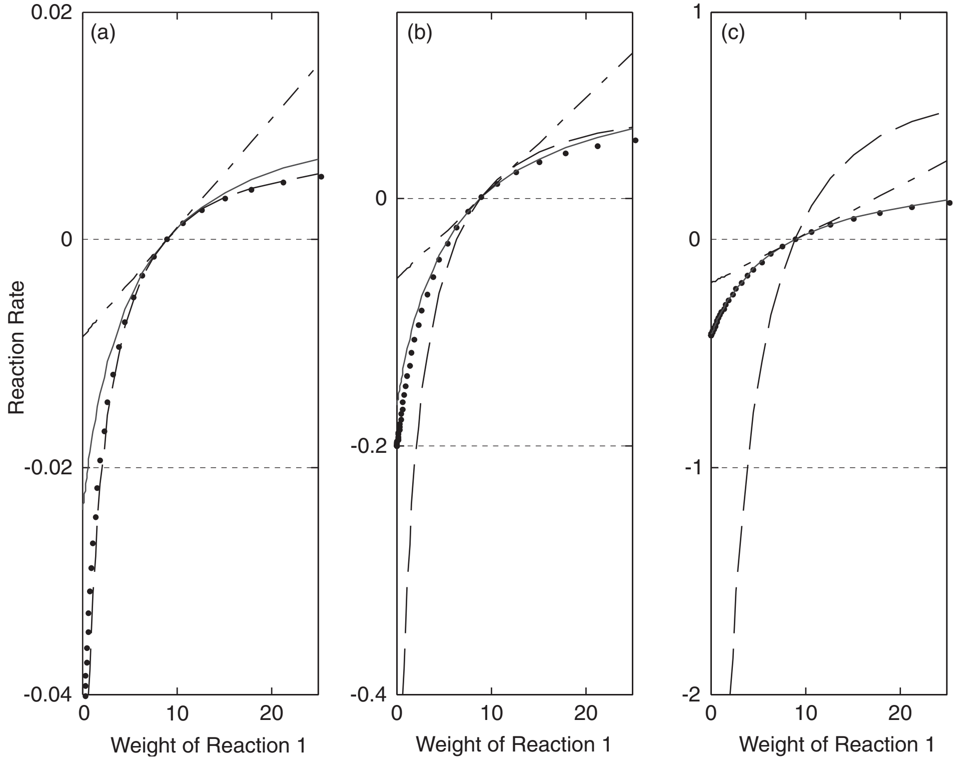

Figure 15 Overall reaction rate and its approximations: step 2 is rate-limiting. Dots represent the exact reaction rate dependence, solid line is the first-term hypergeometric approximation, dashed line corresponds to the reaction-rate equation that assumes the limitation of step 2 and dash-dots represent the equilibrium approximation. Hypergeometric approximation "survives" the 100-times increase in rate-limiting stage kinetic parameters and it works when there is no rate-limiting step at all. Parameters: $r_1 = 5$, $f_3 = 15$, $r_3 = 10$; $r_2 = 0.2$, $f_2 = 0.1$ (a); $r_2 = 2$, $f_2 = 1$ (b); $r_2 = 20$, $f_2 = 10$, (c).

increasing part of dependence. The hypergeometric approximation (we used just the first-term approximation, i.e. $R = -(B_0)/(B_1)$ works for all listed cases within the convergence boundaries.

Thus, when applicable, the hypergeometric approximation covers all classical cases. It is obvious advantage for the situations where we do not have the clear hierarchy of reaction rate parameters.

4. DISCUSSION AND CONCLUSIONS

We consider that there was a step towards to the development of the general theoretical description of kinetic behavior of complex reactions which covers many parametric domains, particularly domains on "both sides" of the chemical equilibrium, domains with step limiting, regions of the vicinity of the

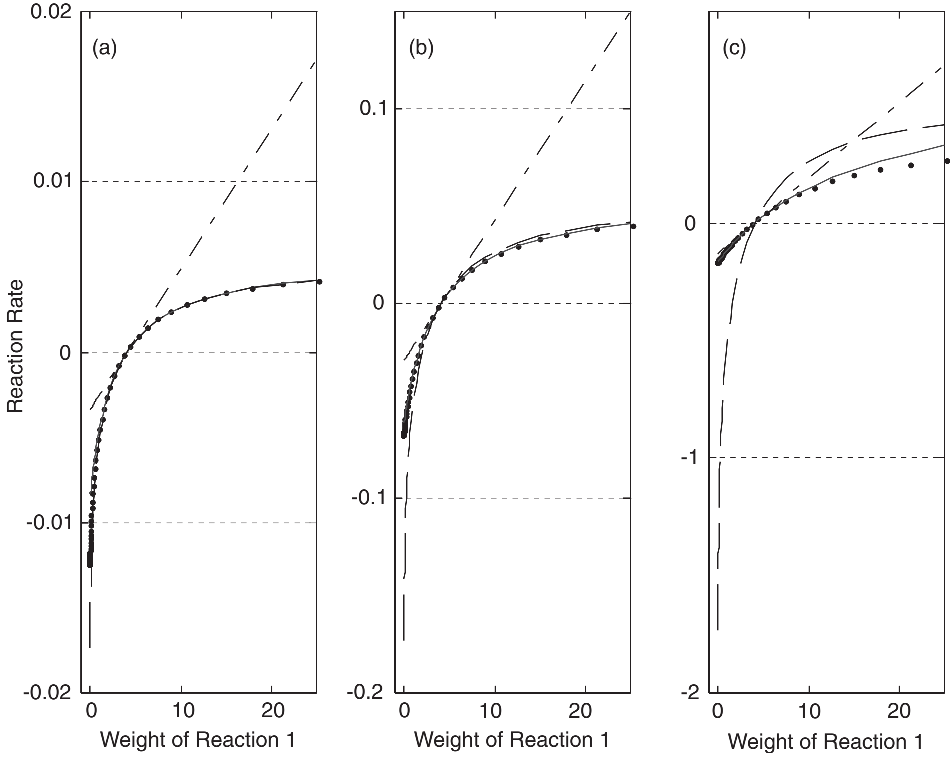

Figure 16 Overall reaction rate and its approximations: step 3 is rate-limiting. Parameters: $r_1 = 2$, $f_2 = 14$, $r_2 = 10$; $r_3 = 0.2$, $f_3 = 0.1$ (a); $r_3 = 2$, $f_3 = 1$ (b); $r_3 = 20$, $f_3 = 10$ (c). See Figure 15 for notation and comments.

equilibrium, and even domains, in which the branch of overall reaction rate is not unique ("multiplicity of steady states"). The developed mathematical constructions, i.e. *kinetic polynomial* and its analytical solution as a hypergeometric series, describe all these domains. Validity of these constructions is rigorously justified based on recent advanced results of the algebraic theory (Gel'fand–Kapranov–Zelevinsky's and Sturmfels' results). In our approach, the concept of ensemble of equilibrium subsystems introduced in our earlier papers (see in detail Lazman and Yablonskii, 1991) was used as a very efficient tool of mathematical analysis and physico-chemical understanding. The equilibrium subsystem is such a system that corresponds to the following assumption: (n−1) steps are considered to be under equilibrium conditions, one step is limiting, where n is a number of steps. In fact, the concept of "equilibrium subsystems" is a generalization of the concept of "equilibrium step", which is well-known in chemical kinetics. Then, we take n of these equlibrium subsystems ("an ensemble of equilibrium subsystems"). It was shown that solutions of these subsystems ("roots", "all roots", not just one "root") define coefficients of the kinetic polynomial.

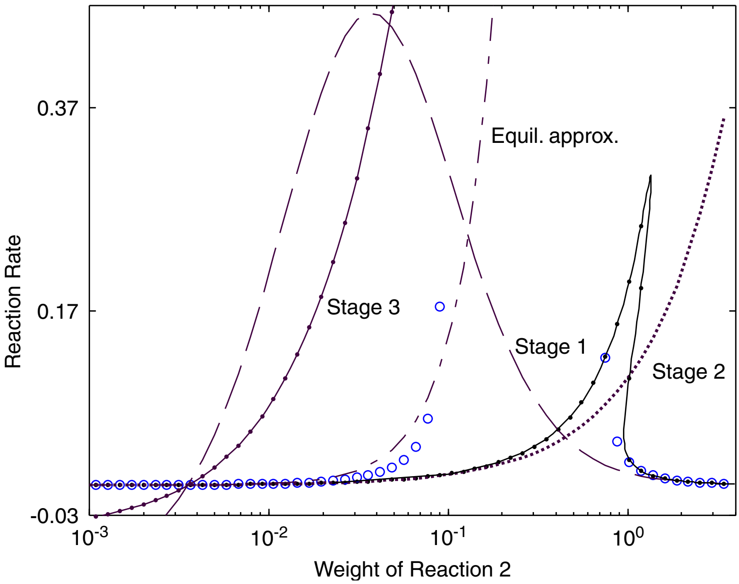

Figure 17 Overall reaction rate, its classic approximations and its hypergeometric approximation (circles): LH mechanism.

In the future, such algebraic representations can be constructed and analyzed for more complex mechanisms, e.g. two-route mechanisms, mechanisms with two sites of active centers, etc. It is quite interesting that the hypergeometric representation describes also the "low-rate" branch, which is located in the domain "very far" from the equilibrium.

Applying "kinetic polynomial" approach we found the analytical representation for the "thermodynamic branch" of the overall reaction rate of the complex reaction *with no traditional assumptions on the rate limiting and "fast" equilibrium of steps*.

The obtained explicit equation, "four-term equation", can be presented in a simple manner as follows:

$$R = \frac{k_+(f_+(c) - K_{\text{eq}}^{-1} f_-(c))}{\sum(k,c)} N(k,c) \tag{77}$$

This equation can be used for a description of kinetic behavior of steady-state open catalytic systems as well as quasi (pseudo)-steady-state catalytic systems, both closed and open.

Equation (77) has four terms:

(1) *an apparent kinetic coefficient* k_+; (2) *a "potential term"* $(f_+(c) - K_{\text{eq}}^{-1} f_-(c))$ related to the net reaction ("driving force" of irreversible thermodynamics); (3) a *"resistance" term,* $\Sigma(k,c)$, denominator of the polynomial type, which reflects complexity of chemical reaction, both its non-elementarity (many-step character) and non-linearity of elementary steps as well; (4) finally, *the "fourth term"*, $N(k,c)$, a polynomial in concentrations and kinetic parameters. This fourth term is

generated exclusively by the non-linearity of reaction steps. This term is the main distinguishing feature of the general equation (77) in comparison with LHHW equations based on simplifying assumptions.

In the absence of non-linear steps the ''fourth'' term is also absent.

The interesting feature of our representation is that many sub-terms of the ''fourth'', non-linear, term may contain the ''potential term'' (the cyclic characteristic C) as well. It means that even in the domain ''far from equilibrium'' the open system still may have a ''memory'' about the equilibrium. Particular forms of this general Equation (77), i.e. for the cases of step limiting and the vicinity of equilibrium, respectively, are presented.

These explicit forms do not contain the ''fourth term''.

The obtained result gives a desired answer regarding the validity of the Horiuti–Boreskov form. So, the presentation of the overall reaction rate of the complex reaction as a difference between two terms, overall rates of forward and backward reactions respectively, is valid, if we are able to present this rate in the form of Equation (77). We can propose a reasonable hypothesis (it has to be proven separately) that it is always possible even for the non-linear mechanism, if the ''physical'' branch of reaction rate is unique, i.e. multiplicity of steady states is not observed. As it has been proven for the MAL systems, the steady state is unique, if the detailed mechanism of surface catalytic reaction does not include the step of interaction between the different surface intermediates (Yablonskii et al., 1991). This hypothesis will be analyzed in further studies.

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APPENDIX 1. REACTION OVERALL RATE EQUATIONS FOR LINEAR MECHANISMS

A. Two-stage mechanism of water–gas shift reaction

$$\begin{array}{l} 1.\quad Z + H_2O \Leftrightarrow ZO + H_2 \\ 2.\quad ZO + CO \Leftrightarrow Z + CO_2 \\ \hline \quad H_2O + CO \Leftrightarrow H_2 + CO_2 \end{array}$$

Overall reaction rate is

$$R = \frac{K^+ c_{H_2O} c_{CO} - K^- c_{H_2} c_{CO_2}}{\sum}$$

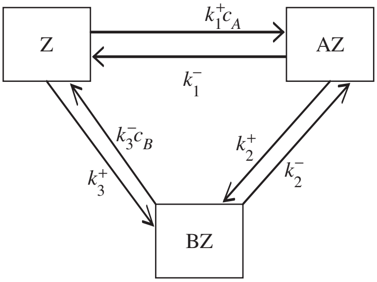
where

$$K^+ = k_1^+ k_2^+, \qquad K^- = k_1^- k_2^-, \qquad \sum = k_1^+ c_{H_2O} + k_2^+ c_{CO} + k_1^- c_{H_2} + k_2^- c_{CO_2},$$

$$R^+ = \frac{K^+ c_{H_2O} c_{CO}}{\sum}, \quad R^- = \frac{K^- c_{H_2} c_{CO_2}}{\sum}, \quad \frac{R^+}{R^-} = K_{eq} \frac{c_{H_2O} c_{CO}}{c_{H_2} c_{CO_2}}$$

B. Three-stage mechanism of catalytic isomerization

$$\begin{array}{l} 1.\quad A + Z \Leftrightarrow AZ \\ 2.\quad AZ \Leftrightarrow BZ \\ 3.\quad BZ \Leftrightarrow B + Z \\ \hline \qquad A \Leftrightarrow B \end{array}$$



Overall reaction rate is

$$R = \frac{K^{+}c_{\mathrm{A}} - K^{-}c_{\mathrm{B}}}{\sum}$$

where

$$\begin{array}{lll}
K^{+} = k_1^{+}k_2^{+}k_3^{+}, & K^{-} = k_1^{-}k_2^{-}k_3^{-}, & \sum = K_1c_{\mathrm{A}} + K_2c_{\mathrm{B}} + K_3, \\
K_1 = k_1^{+}(k_2^{+} + k_3^{+} + k_2^{-}), & K_2 = k_3^{-}(k_2^{+} + k_2^{-} + k_1^{-}), & K_3 = k_2^{+}k_3^{+} + k_1^{-}k_2^{-} + k_1^{-}k_3^{+} \\
R^{+} = \dfrac{K^{+}c_{\mathrm{A}}}{\sum}, & R^{-} = \dfrac{K^{-}c_{\mathrm{B}}}{\sum}, & \dfrac{R^{+}}{R^{-}} = K_{\mathrm{eq}}\dfrac{c_{\mathrm{A}}}{c_{\mathrm{B}}}
\end{array}$$

APPENDIX 2. COMPUTER GENERATED “BRACKETS” FOR 4TH DEGREE POLYNOMIAL

Formulas correspond to the upper boundary of m for each independent index in the summation (56).

$\left[\dfrac{B_0}{B_1}\right]$, $m = 3$:

$$\begin{aligned}
&-414,414,000\frac{B_0^{19}B_2^3B_3^3B_4^3}{B_1^{28}} - \frac{33,649,000B_0^{18}B_2^2B_3^3B_4^3}{B_1^{26}} - \frac{2,018,940B_0^{17}B_2B_3^3B_4^3}{B_1^{24}} \\
&\quad + \frac{24,227,280B_0^{17}B_2^3B_3^2B_4^3}{B_1^{25}} - \frac{67,830B_0^{16}B_3^3B_4^3}{B_1^{22}} + \frac{2,238,390B_0^{16}B_2^2B_3^2B_4^3}{B_1^{23}} \\
&\quad - \frac{17,160,990B_0^{16}B_2^3B_3^3B_4^2}{B_1^{24}} + \frac{155,040B_0^{15}B_2B_3^2B_4^3}{B_1^{21}} - \frac{1,085,280B_0^{15}B_2^3B_3B_4^3}{B_1^{22}} \\
&\quad - \frac{1,627,920B_0^{15}B_2^2B_3^3B_4^2}{B_1^{22}} + \frac{6,120B_0^{14}B_3^2B_4^3}{B_1^{19}} - \frac{116,280B_0^{14}B_2^2B_3B_4^3}{B_1^{20}} \\
&\quad - \frac{116,280B_0^{14}B_2B_3^3B_4^2}{B_1^{20}} + \frac{1,162,800B_0^{14}B_2^3B_3^2B_4^2}{B_1^{21}} - \frac{9,520B_0^{13}B_2B_3B_4^3}{B_1^{18}} \\
&\quad - \frac{4,760B_0^{13}B_3^3B_4^2}{B_1^{18}} + \frac{28,560B_0^{13}B_2^3B_4^3}{B_1^{19}} + \frac{128,520B_0^{13}B_2^2B_3^2B_4^2}{B_1^{19}} \\
&\quad - \frac{542,640B_0^{13}B_2^3B_3^3B_4}{B_1^{20}} - \frac{455B_0^{12}B_3B_4^3}{B_1^{16}} + \frac{3,640B_0^{12}B_2^2B_4^3}{B_1^{17}} \\
&\quad + \frac{10,920B_0^{12}B_2B_3^2B_4^2}{B_1^{17}} - \frac{61,880B_0^{12}B_2^3B_3B_4^2}{B_1^{18}} - \frac{61,880B_0^{12}B_2^2B_3^3B_4}{B_1^{18}} \\
&\quad + \frac{364B_0^{11}B_2B_4^3}{B_1^{15}} + \frac{546B_0^{11}B_3^2B_4^2}{B_1^{15}} - \frac{8,190B_0^{11}B_2^2B_3B_4^2}{B_1^{16}} \\
&\quad - \frac{5,460B_0^{11}B_2B_3^3B_4}{B_1^{16}} + \frac{43,680B_0^{11}B_2^3B_3^2B_4}{B_1^{17}} + \frac{22B_0^{10}B_4^3}{B_1^{13}} - \frac{858B_0^{10}B_2B_3B_4^2}{B_1^{14}} \\
&\quad - \frac{286B_0^{10}B_3^3B_4}{B_1^{14}} + \frac{2,002B_0^{10}B_2^3B_4^2}{B_1^{15}} + \frac{6,006B_0^{10}B_2^2B_3^2B_4}{B_1^{15}}
\end{aligned}$$

$$
\begin{aligned}
&-\frac{10,010B_0^{10}B_2^3B_3^3}{B_1^{16}}-\frac{55B_0^9B_3B_4^2}{B_1^{12}}+\frac{330B_0^9B_2^2B_4^2}{B_1^{13}}+\frac{660B_0^9B_2B_3^2B_4}{B_1^{13}}\\
&-\frac{2,860B_0^9B_2^3B_3B_4}{B_1^{14}}-\frac{1,430B_0^9B_2^2B_3^3}{B_1^{14}}+\frac{45B_0^8B_2B_4^2}{B_1^{11}}+\frac{45B_0^8B_3^2B_4}{B_1^{11}}\\
&-\frac{495B_0^8B_2^2B_3B_4}{B_1^{12}}-\frac{165B_0^8B_2B_3^3}{B_1^{12}}+\frac{990B_0^8B_2^3B_3^2}{B_1^{13}}+\frac{4B_0^7B_4^2}{B_1^9}\\
&-\frac{72B_0^7B_2B_3B_4}{B_1^{10}}-\frac{12B_0^7B_3^3}{B_1^{10}}+\frac{120B_0^7B_2^3B_4}{B_1^{11}}+\frac{180B_0^7B_2^2B_3^2}{B_1^{11}}-\frac{7B_0^6B_3B_4}{B_1^8}\\
&+\frac{28B_0^6B_2^2B_4}{B_1^9}+\frac{28B_0^6B_2B_3^2}{B_1^9}-\frac{84B_0^6B_2^3B_3}{B_1^{10}}+\frac{6B_0^5B_2B_4}{B_1^7}+\frac{3B_0^5B_3^2}{B_1^7}\\
&-\frac{21B_0^5B_2^2B_3}{B_1^8}+\frac{B_0^4B_4}{B_1^5}-\frac{5B_0^4B_2B_3}{B_1^6}+\frac{5B_0^4B_2^3}{B_1^7}-\frac{B_0^3B_3}{B_1^4}+\frac{2B_0^3B_2^2}{B_1^5}+\frac{B_0^2B_2}{B_1^3}+\frac{B_0}{B_1}
\end{aligned}
$$

$\left[\dfrac{B_1}{B_2}\right]$, $m = 3$:

$$
\begin{aligned}
&92,400\frac{B_0^3B_1^4B_3^3B_4^3}{B_2^{13}}+\frac{8,400B_0^3B_1^3B_3^2B_4^3}{B_2^{11}}+\frac{560B_0^3B_1^2B_3B_4^3}{B_2^9}\\
&\quad-\frac{2,520B_0^3B_1^2B_3^3B_4^2}{B_2^{10}}+\frac{20B_0^3B_1B_4^3}{B_2^7}-\frac{210B_0^3B_1B_3^2B_4^2}{B_2^8}\\
&\quad-\frac{120,120B_0^2B_1^6B_3^3B_4^3}{B_2^{14}}-\frac{13,860B_0^2B_1^5B_3^2B_4^3}{B_2^{12}}-\frac{1,260B_0^2B_1^4B_3B_4^3}{B_2^{10}}\\
&\quad+\frac{6,300B_0^2B_1^4B_3^3B_4^2}{B_2^{11}}-\frac{70B_0^2B_1^3B_4^3}{B_2^8}+\frac{840B_0^2B_1^3B_3^2B_4^3}{B_2^9}+\frac{90B_0^2B_1^2B_3B_4^2}{B_2^7}\\
&\quad-\frac{210B_0^2B_1^2B_3^3B_4}{B_2^8}+\frac{6B_0^2B_1B_4^2}{B_2^5}-\frac{30B_0^2B_1B_3^2B_4}{B_2^6}+\frac{60,060B_0B_1^8B_3^3B_4^3}{B_2^{15}}\\
&\quad+\frac{7,920B_0B_1^7B_3^2B_4^3}{B_2^{13}}+\frac{840B_0B_1^6B_3B_4^3}{B_2^{11}}-\frac{4,620B_0B_1^6B_3^3B_4^2}{B_2^{12}}+\frac{56B_0B_1^5B_4^3}{B_2^9}\\
&\quad-\frac{756B_0B_1^5B_3^2B_4^2}{B_2^{10}}-\frac{105B_0B_1^4B_3B_4^2}{B_2^8}+\frac{280B_0B_1^4B_3^3B_4}{B_2^9}-\frac{10B_0B_1^3B_4^2}{B_2^6}\\
&\quad+\frac{60B_0B_1^3B_3^2B_4}{B_2^7}+\frac{12B_0B_1^2B_3B_4}{B_2^5}-\frac{10B_0B_1^2B_3^3}{B_2^6}+\frac{2B_0B_1B_4}{B_2^3}-\frac{3B_0B_1B_3^2}{B_2^4}\\
&\quad-\frac{10,010B_1^{10}B_3^3B_4^3}{B_2^{16}}-\frac{1,430B_1^9B_3^2B_4^3}{B_2^{14}}-\frac{165B_1^8B_3B_4^3}{B_2^{12}}+\frac{990B_1^8B_3^3B_4^2}{B_2^{13}}\\
&\quad-\frac{12B_1^7B_4^3}{B_2^{10}}+\frac{180B_1^7B_3^2B_4^2}{B_2^{11}}+\frac{28B_1^6B_3B_4^2}{B_2^9}-\frac{84B_1^6B_3^3B_4}{B_2^{10}}+\frac{3B_1^5B_4^2}{B_2^7}\\
&\quad-\frac{21B_1^5B_3^2B_4}{B_2^8}-\frac{5B_1^4B_3B_4}{B_2^6}+\frac{5B_1^4B_3^3}{B_2^7}-\frac{B_1^3B_4}{B_2^4}+\frac{2B_1^3B_3^2}{B_2^5}+\frac{B_1^2B_3}{B_2^3}+\frac{B_1}{B_2}
\end{aligned}
$$

$\left[\frac{B_2}{B_3}\right]$, $m = 10$:

$$\begin{aligned}
&2,002\frac{B_0^3B_2^2B_4^{10}}{B_3^{15}} + \frac{220B_0^3B_2B_4^9}{B_3^{13}} + \frac{6,006B_0^2B_1^2B_2B_4^{10}}{B_3^{15}} - \frac{30,030B_0^2B_1B_2^3B_4^{10}}{B_3^{16}} \\
&\quad - \frac{4,290B_0^2B_1B_2^2B_4^9}{B_3^{14}} - \frac{495B_0^2B_1B_2B_4^8}{B_3^{12}} + \frac{24,024B_0^2B_2^5B_4^{10}}{B_3^{17}} \\
&\quad + \frac{5,005B_0^2B_2^4B_4^9}{B_3^{15}} + \frac{990B_0^2B_2^3B_4^8}{B_3^{13}} + \frac{180B_0^2B_2^2B_4^7}{B_3^{11}} + \frac{28B_0^2B_2B_4^6}{B_3^9} \\
&\quad - \frac{30,030B_0B_1^3B_2^2B_4^{10}}{B_3^{16}} - \frac{2,860B_0B_1^3B_2B_4^9}{B_3^{14}} + \frac{120,120B_0B_1^2B_2^4B_4^{10}}{B_3^{17}} \\
&\quad + \frac{20,020B_0B_1^2B_2^3B_4^9}{B_3^{15}} + \frac{2,970B_0B_1^2B_2^2B_4^8}{B_3^{13}} + \frac{360B_0B_1^2B_2B_4^7}{B_3^{11}} \\
&\quad - \frac{136,136B_0B_1B_2^6B_4^{10}}{B_3^{18}} - \frac{30,030B_0B_1B_2^5B_4^9}{B_3^{16}} - \frac{6,435B_0B_1B_2^4B_4^8}{B_3^{14}} \\
&\quad - \frac{1,320B_0B_1B_2^3B_4^7}{B_3^{12}} - \frac{252B_0B_1B_2^2B_4^6}{B_3^{10}} - \frac{42B_0B_1B_2B_4^5}{B_3^8} + \frac{43,758B_0B_2^8B_4^{10}}{B_3^{19}} \\
&\quad + \frac{11,440B_0B_2^7B_4^9}{B_3^{17}} + \frac{3,003B_0B_2^6B_4^8}{B_3^{15}} + \frac{792B_0B_1^5B_4^7}{B_3^{13}} + \frac{210B_0B_2^4B_4^6}{B_3^{11}} \\
&\quad + \frac{56B_0B_2^3B_4^5}{B_3^9} + \frac{15B_0B_2^2B_4^4}{B_3^7} + \frac{4B_0B_2B_4^3}{B_3^5} - \frac{3,003B_1^5B_2B_4^{10}}{B_3^{16}} \\
&\quad + \frac{40,040B_1^4B_2^3B_4^{10}}{B_3^{17}} + \frac{5,005B_1^4B_2^2B_4^9}{B_3^{15}} + \frac{495B_1^4B_2B_4^8}{B_3^{13}} - \frac{136,136B_1^3B_2^5B_4^{10}}{B_3^{18}} \\
&\quad - \frac{25,025B_1^3B_2^4B_4^9}{B_3^{16}} - \frac{4,290B_1^3B_2^3B_4^8}{B_3^{14}} - \frac{660B_1^3B_2^2B_4^7}{B_3^{12}} - \frac{84B_1^3B_2B_4^6}{B_3^{10}} \\
&\quad + \frac{175,032B_1^2B_2^7B_4^{10}}{B_3^{19}} + \frac{40,040B_1^2B_2^6B_4^9}{B_3^{17}} + \frac{9,009B_1^2B_2^5B_4^8}{B_3^{15}} + \frac{1,980B_1^2B_2^4B_4^7}{B_3^{13}} \\
&\quad + \frac{420B_1^2B_2^3B_4^6}{B_3^{11}} + \frac{84B_1^2B_2^2B_4^5}{B_3^9} + \frac{15B_1^2B_2B_4^4}{B_3^7} - \frac{92,378B_1B_2^9B_4^{10}}{B_3^{20}} \\
&\quad - \frac{24,310B_1B_2^8B_4^9}{B_3^{18}} - \frac{6,435B_1B_2^7B_4^8}{B_3^{16}} - \frac{1,716B_1B_2^6B_4^7}{B_3^{14}} - \frac{462B_1B_2^5B_4^6}{B_3^{12}} \\
&\quad - \frac{126B_1B_2^4B_4^5}{B_3^{10}} - \frac{35B_1B_2^3B_4^4}{B_3^8} - \frac{10B_1B_2^2B_4^3}{B_3^6} - \frac{3B_1B_2B_4^2}{B_3^4} + \frac{16,796B_2^{11}B_4^{10}}{B_3^{21}} \\
&\quad + \frac{4,862B_2^{10}B_4^9}{B_3^{19}} + \frac{1,430B_2^9B_4^8}{B_3^{17}} + \frac{429B_2^8B_4^7}{B_3^{15}} + \frac{132B_2^7B_4^6}{B_3^{13}} + \frac{42B_2^6B_4^5}{B_3^{11}} \\
&\quad + \frac{14B_2^5B_4^4}{B_3^9} + \frac{5B_2^4B_4^3}{B_3^7} + \frac{2B_2^3B_4^2}{B_3^5} + \frac{B_2^2B_4}{B_3^3} + \frac{B_2}{B_3}
\end{aligned}$$

APPENDIX 3. PROOF OF PROPOSITION 3.

By formula (40)

$$\frac{B_1}{B_0} = -\sum_{k=1}^{n} \nu_k S_k,$$

$$S_k = \sum_{j_k=1}^{M_k} \frac{1}{w_k(j_k)}$$

where $w_k(j_k)$ is the value of the rate of stage with index k calculated at zero with index j_k of the system (27) at $R = 0$. These zeros could be *boundary* (i.e. $z_l = 0$ for some $1 \le l \le n$) and *interior* (otherwise). Note, that system (27) always has the interior (toric) roots and may or may not have the boundary roots. Consider some $S_k : \nu_k \neq 0$. We can present it as

$$S_k = S_k^B + S_k^I \tag{A3.1}$$

where $S_k^B = \sum_{j\in B} 1/w_k(j)$, $S_k^I = \sum_{j\in I} 1/w_k(j)$ and B and I are the sets of boundary and interior zeros.

It follows from Lemma 14.3 (see Bykov et al., 1998) that in the case $\nu_k \neq 0$ we have $w_k(j) = f_k z^{\alpha^k} \neq 0$ or $w_k(j) = r_k z^{\beta^k} \neq 0$ i.e. $w_k\ (j)$ is generically non-zero and finite in the point of equilibrium.[23] Thus, S_k^B cannot have C^m, $m \neq 0$ as a factor.

There are $|\Delta_k|$ interior zeroes (see Bykov et al., 1998). They can be subdivided into p groups, each group producing the multiplier C in the coefficient B_0 (see proof of the Theorem 14.1, Bykov et al., 1998). We can write S_k^I as

$$S_k^I = \frac{\sum_{l=1}^{p} \sum_{j\in I_l} \prod_{i\in I[l]} w_k(i) \cdot \prod_{i\in I_l\ i\neq j} w_k(i)}{\prod_{j\in I} w_k(j)} \tag{A3.2}$$

where I_l is lth group. Let $c = (\prod_{i=1}^{n} (f_i/r_i)^{\nu_i} - 1)$, ν_i is defined as in Proposition 1 and let $w_{-k}(j) = r_k z(j)^{\beta^k}$. Then

$$S_k^I = (-1)^{\nu_k - 1} \frac{\sum_{l=1}^{p} \prod_{i\in I[l]} w_{-k}(i) \prod_{i\in I_l, i\neq j} w_k(i)}{c \prod_{j\in I} w_{-k}(j)} \tag{A3.3}$$

There are exactly p interior zeroes $\mathbf{z}(j_l^{\mathrm{eq}})$, $l = 1, \ldots, p$ such that $w_k(j_l^{\mathrm{eq}})$ vanishes at the equilibrium. At the equilibrium

$$\prod_{i\neq j_l^{\mathrm{eq}}} w_k(i) = (-1)^{\nu_k - 1} \nu_k \prod_{i\neq j_l^{\mathrm{eq}}} w_{-k}(i)$$

---

[23] This follows from the formula for solution $z_l\ (j)$ for non-zero z_l (see Lemma 14.1 in Bykov et al., 1998).

and at the vicinity of equilibrium (i.e. at $c \to 0$) we have

$$S_k^I|_{\text{eq}} \cong \frac{\nu_k}{c}\sum_{l=1}^{p}\frac{1}{w_{-k}(j_l^{\text{eq}})} \tag{A3.4}$$

As S_k^B is finite, in the neighborhood of equilibrium we have

$$S_k|_{\text{eq}} \cong S_k^I|_{\text{eq}}$$

Now, it is sufficient to prove that $y_k = \sum_{l=1}^{p}(1/w_{-k}(j_l^{\text{eq}})) \neq 0$ and finite at the equilibrium. This will ensure that y_k cannot produce additional c-factors, so that $(B_0)/(B_1) \sim 1/C$ which means that $B_1 \sim C^{p-1}$ (see Propositions 1 and 2). It is obvious that $y_k > 0$ if $p = 1$ (the only root of system (27) is positive at $R = 0$). Let us prove this for the case of $p \geq 1$.

Lemma $y_k > 0$ *and finite*

We may assume $k = 1$. Let $w_{1\text{eq}} = w_{-1}(j_1^{\text{eq}}) \equiv w_1(j_1^{\text{eq}})$. Applying the explicit formula for interior roots (see Bykov et al., 1998; Lazman and Yablonskii, 1991), we have[24]

$$\frac{1}{w_{1\text{eq}}} = \frac{1}{f_1}\left[\sum_{l=1}^{n}\prod_{j=2}^{n}\kappa_j^{-\frac{\Delta_{jl}^1}{p_1\Delta_1}}\cdot\exp\left(2\pi i\sum_{j=2}^{n}m_j\frac{\Delta_{jl}^1}{p_1\Delta_1}\right)\right]^{p_1} \tag{A3.5}$$

We can define integers m_j, $\quad j = 2, \ldots, n$ as (see Bykov et al., 1998, p. 145)

$$\begin{gathered} m_j = \nu_1 q m_j^0, \qquad q = 0,\ \nu_1, \ldots, (p-1)\nu_1, \\ m_1^0\nu_1 + \cdots + m_n^0\nu_n = -1 \end{gathered} \tag{A3.6}$$

Remind that ν_1 belongs to the set of relatively prime stoichiometric numbers, so that

$$\Delta_1 = p\nu_1 \tag{A3.7}$$

Taking into account Equations (A3.5) and (A3.6) we can write

$$\sum_{l=1}^{p}\frac{1}{w_{1\text{eq}}} = \frac{1}{f_1}\sum_{q}\left[\sum_{l=1}^{n}\prod_{j=2}^{n}\kappa_j^{-\frac{\Delta_{jl}^1}{p_1 p\nu_1}}\cdot\exp\left(2\pi i q\sum_{j=2}^{n}m_j^0\frac{\Delta_{jl}^1}{p_1 p}\right)\right]^{p_1}, \qquad q = 0,\ \nu_1, \ldots, (p-1)\nu_1 \tag{A3.8}$$

Let us now expand the [] in Equation (A3.8) and consider one of the expansion terms

$$T = C_a t_1^{a_1}\cdot\ldots\cdot t_n^{a_n}, \quad \|a\| = p_1$$

---

[24] Notation is the same as in formula (52), (see Section 3.1.1).

We have

$$T = C_a \prod_{j=2}^{n} \kappa_j^{-\frac{\mu_j}{p_1 p \nu_1}} \cdot \exp\left(2\pi i q \frac{\sum\limits_{j=2}^{n} m_j^0 \mu_j}{p_1 p} \right) \tag{A3.9}$$

where

$$\mu_j = \left| \begin{array}{ccc} \alpha_{11} & \cdots & \alpha_{1n} \\ \vdots & \gamma & \vdots \\ a_1 & \{row\ j\} & a_n \\ & \gamma & \end{array} \right| = p_1 \mu_j^0 \tag{A3.10}$$

The property (A3.10) becomes obvious after adding up the columns (all sums are 0 except sums in rows 1 and j where they are equal to p_1). Collecting all terms corresponding to the term T for all values of q we have

$$\sum_{q=0}^{p-1} T_q = C_a \prod_{j=2}^{n} \kappa_j^{-\frac{\mu_j^0}{p \nu_1}} s$$

where

$$s = 1 + g + \cdots + g^{p-1},$$

$$g = \exp\left(2\pi i \frac{\sum\limits_{j=2}^{n} m_j^0 \mu_j^0}{p} \right)$$

We have

$$s = \begin{cases} p, & \text{if } p \text{ divides} \sum\limits_{j=2}^{n} m_j^0 \mu_j^0 \\ 0, & \text{otherwise} \end{cases}$$

Thus, $s \geq 0$. However $\mu_j^0 = 0$ if $\alpha_{11} = a_1, \ldots, \alpha_{1n} = a_n$. Thus, we have strictly positive addendum that proves the Lemma.

In the vicinity of equilibrium we have

$$-\frac{B_0}{B_1} \cong \frac{\prod\limits_{i=1}^{n} (f_i/r_i)^{\nu_i} - 1}{\sum\limits_{k=1}^{n} \nu_k^2 \sum\limits_{l=1}^{p} 1/w_{-k}(j_l^{\mathrm{eq}})} \tag{A3.11}$$

and the denominator of Equation (A3.11) is strictly positive at the equilibrium.

Note that Equation (A3.11) produces formula (53) for the overall reaction rate at the linear vicinity of thermodynamic equilibrium. Formula (53) follows from Equation (A3.11) when $p = 1$.

APPENDIX 4. THERMODYNAMIC BRANCH IS FEASIBLE

We are going to show that in the vicinity of equilibrium, the thermodynamic branch (66), corresponds to the feasible solution of system (21) (i.e. solution with $z_j > 0,\ j = 1, ..., n$).

Proposition A4.1. System (21) can have one and only one feasible zero with $R = 0$[25] if

$$f_1^{\nu_1}, \ldots, f_n^{\nu_n} = r_1^{\nu_1}, \ldots, r_n^{\nu_n} \tag{A4.0}$$

Proof. At the equilibrium, $z_1, \ldots, z_n$ should solve equilibrium subsystem (27). Let $s = 1$.

Interior solutions of equilibrium subsystem satisfy the following relations (see Bykov et al., 1998, p. 144)

$$\begin{gathered} z_1 = z_n \mathbf{C}^{\Delta^1/\Delta_1} \mathrm{e}^{2\pi i < \mathbf{m}, \Delta^1/\Delta_1 >}, \\ \vdots \\ z_{n-1} = z_n \mathbf{C}^{\Delta^{n-1}/\Delta_1} \mathrm{e}^{2\pi i < \mathbf{m}, \Delta^{n-1}/\Delta_1 >}, \\ z_1 + \ldots + z_n = 1 \end{gathered} \tag{A4.1}$$

where $\Delta_1 = \det \Gamma_1, \Gamma_1 = (\alpha_j^s - \beta_j^s)_{j=1,\ldots,n-1}^{s=2,\ldots,n}$, $\Delta^j = (\Delta_2^j, ..., \Delta_n^j)$ is vector of co-factors of the elements of jth column of matrix Γ_1, $\mathbf{C} = (f_2/r_2, ..., f_n/r_n)$ and $\mathbf{m} = (m_2, \ldots, m_n)$ is some integer vector.

The only feasible solution of Equation (A4.1) is

$$z_i = z_n K^{\Delta^i/\Delta_1}, \qquad z_n = 1/(1 + K^{\Delta^1/\Delta_1} + K^{\Delta^{n-1}/\Delta_1}) \tag{A4.2}$$

At the equilibrium, we have

$$f_1 z^{\alpha^1} = r_1 z^{\beta^1} \tag{A4.3}$$

Substituting Equation (A4.2) into Equation (A4.3) we have the following necessary and sufficient condition of the equilibrium

$$\mathrm{K}_{\mathrm{eq}} = 1 \tag{A4.4}$$

where

$$\mathrm{K}_{\mathrm{eq}} = (f_1/r_1)(f_2/r_2)^{\nu_2/\nu_1}, \ldots, (f_n/r_n)^{\nu_n/\nu_1} \tag{A4.5}$$

---

[25] Equilibrium point is unique, as expected from thermodynamics of ideal systems.

Conditions (A4.2) and (A4.4) (it is equivalent to the condition (A4.0) for feasible values of f_i, r_i) are necessary and sufficient conditions for $z_1 > 0, \ldots, z_n > 0$ to solve the system (21).

Proposition A4.2. Thermodynamic branch $R = -[(B_0)/(B_1)]$ corresponds to the feasible solution in the vicinity of equilibrium.

(i) Let $p = 1$ (see Propositions 1 and 2). Equilibrium subsystem (21), corresponding to $s = 1$, has $|\Delta_1|$ interior solutions (see Lemma 14.1 in Bykov et al., 1998).

If $p = 1$, $|\Delta_1| = \nu_1$. It follows from Equation (A4.4) that at the equilibrium each of these ν_1 solutions should satisfy condition

$$\mathrm{K_{eq}} \mathrm{e}^{2\pi i (j/\nu_1)} = 1, \qquad j = 0, 1, \ldots, \nu_1 - 1 \tag{A4.6}$$

(for details of obtaining formula (A4.6) see proof of Proposition 1, Lazman and Yablonskii (1991) and Bykov et al., 1998).

For $\mathrm{K_{eq}} > 0$, condition (A4.6) could be satisfied only, if $j = 0$. There is a bijection between solution (A4.1) and condition (A4.6), and the case $j = 0$ corresponds to the only feasible solution (A4.2) (see Proposition A4.1). However, when $p = 1$, there is only one branch of solutions of kinetic polynomial vanishing at the equilibrium.[26] As the thermodynamic branch satisfies the equilibrium condition (A4.0) and there are no other branches vanishing at the equilibrium (we proved in Appendix 3 that $B_1 \neq 0$ at the equilibrium (see also Lazman and Yablonskii, 1991), this branch should be feasible. By continuity, this property should be valid in some vicinity of equilibrium.

(ii) Let now $p > 1$. In this case, we have p branches of kinetic polynomial zeros vanishing at the equilibrium. Which one corresponds to the thermodynamic branch?

In the vicinity of equilibrium, the overall reaction rate satisfies Equation (53a), i.e.

$$R = \frac{\prod_{j=1}^{n} \kappa_j^{\nu_j} - 1}{\sum_{k=1}^{n} \nu_k^2 / w_{k_{\mathrm{eq}}}} \tag{A4.7}$$

Formula (A4.7) is valid for $w_{k_{\mathrm{eq}}}$ defined by formula (A3.4). They may correspond to feasible or non-feasible solutions of system (27) at the equilibrium. Let w_k^f is feasible and $w_k^{[f]}$ is non-feasible value of $w_{k_{\mathrm{eq}}}$. For, $k = 1$ we have[27]

$$1/\left|w_1^{[f]}\right| < (1/f_1)\left|\sum \prod\right|^{p_1} \leq (1/f_1)\left(\sum \left|\prod\right|\right)^{p_1} = 1/w_1^f$$

---

[26] By definition of the resultant, every root of kinetic polynomial solves the system and vice versa.

[27] Formula (A3.4) is presented schematically here.

Then,

$$\left|\sum_{k=1}^{n} v_k^2/w_k^{[f]}\right| \leq \sum_{k=1}^{n} v_k^2\Big/|w_k^{[f]}| < \sum_{k=1}^{n} v_k^2\Big/\left|w_k^f\right|.$$

It follows from (A.4.7) that

$$\left|R^{[f]}\right| \geq \left|R^f\right| \qquad \text{(A4.8)}$$

Note that the equal condition in Equation (A4.8) requires the equilibrium (i.e. Equation (A.4.0)). Thus, in the vicinity of the equilibrium, the non-zero absolute value of feasible reaction rate is always smaller than absolute values of reaction rate corresponding to non-feasible solutions vanishing at the equilibrium. Near the equilibrium, these p "small" solutions are close to the roots of the equation (see Lazman and Yablonskii, 1991, in more detail)

$$B_0'C^p + B_1'C^{p-1}R + \cdots + B_pR^p = 0$$

where B_0' and B_1' are defined in Equation (71). Let $R = vC$. Then $\left|v^f\right| < \left|v^{[f]}\right|$ and we are interested in the root of polynomial

$$B_0' + B_1'v + \cdots + B_pv^p = 0 \qquad \text{(A4.9)}$$

with the smallest absolute value. This root vanishes if $B_0' = 0$, which happens for the thermodynamic branch, i.e. $v = -[B_0'/B_1']$.

Example

For mechanism of para–ortho conversion of hydrogen

(1) $H_2(\text{para}) + 2Z \Leftrightarrow 2HZ$
(2) $2HZ \Leftrightarrow H_2(\text{ortho}) + 2Z$

we have $p = 2$. Figure 18 shows both roots of corresponding kinetic polynomial $(r_1 + f_2 - r_2 - f_1)^2R^2 - 2(f_1f_2 - r_1r_2)(r_1 + f + r_2 + f_2)R + (f_1f_2 - r_1r_2)^2$ and their hypergeometric approximations. Note, that the thermodynamic branch converges to the feasible root which absolute value is always smaller than the non-feasible root.

APPENDIX 5. STURMFELS SERIES COINCIDES WITH THE BIRKELAND SERIES FOR THE CASE OF "THERMODYNAMIC BRANCH"

Sturmfels series. It follows from Equations (34) and (35) at $j = 1$ that

$$x = \sum_{i_2=0,\ldots,\,i_n=0}^{\infty} \frac{(-1)^{i_1+1}}{1+i_0}\binom{i_1}{i_2,\ldots,i_n}\cdot\frac{a_0^{1+i_0}\prod_{k=2}^{n} a_k^{i_k}}{a_1^{1+i_1}} \qquad \text{(A5.1)}$$

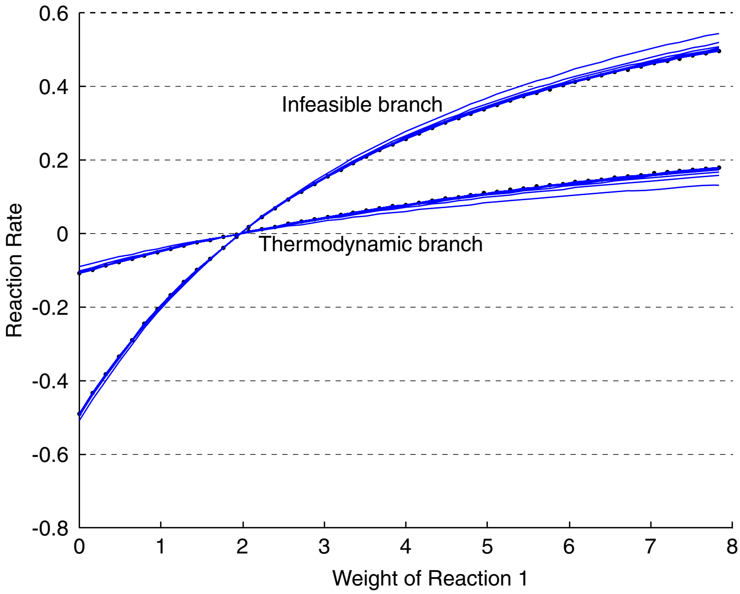


Figure 18 Overall reaction rate and its approximation for the mechanism of hydrogen para–ortho conversion.

where

$$i_0 = \sum_{k=2}^{n} (k-1) i_k, \qquad i_1 = \sum_{k=2}^{n} k i_k$$

Birkeland series. Consider formula (60) at $p = 0$ and $q = 1$. We have

$$\varepsilon = (-1)^{1/(q-p)} = -1,$$

$$-\left\langle \beta_q, k \right\rangle = \sum_{k=2}^{n} i_k k = i_1,$$

$$\left\langle \beta_p, k \right\rangle = \sum_{k=2}^{n} (k-1) i_k = i_0,$$

$$Y_1(b_2, \ldots, b_n) = \sum_{i_2=0,\ldots,\, i_n=0}^{\infty} \frac{(-1)^{1+i_1} \Gamma(1+i_1)}{i_2! \ldots i_n! \;\; \Gamma(1+i_0+1)} \cdot \prod_{k=2}^{n} b_k^{i_k}$$

$$\equiv \sum_{i_2=0,\ldots,\, i_n=0}^{\infty} \frac{(-1)^{1+i_1} i_1!}{i_2! \ldots i_n! \;\; (i_0+1)!} \cdot \prod_{k=2}^{n} b_k^{i_k}$$

$$\equiv \sum_{i_2=0,\ldots,\, i_n=0}^{\infty} \frac{(-1)^{1+i_1} \left(\sum\limits_{k=2}^{n} k i_k \right)!}{(i_0+1) \;\; i_2! \ldots i_n! \left(\sum\limits_{k=2}^{n} k i_k - \sum\limits_{k=2}^{n} i_k \right)!} \cdot \prod_{k=2}^{n} b_k^{i_k}$$

$$\equiv \sum_{i_2=0,\ldots,\, i_n=0}^{\infty} \frac{(-1)^{1+i_1}!}{(i_0+1)} \cdot \begin{pmatrix} i_1 \\ i_2 \ldots i_n \end{pmatrix} \cdot \prod_{k=2}^{n} b_k^{i_k}$$

Then,

$$x = \lambda_1 Y(\lambda_0 \lambda_1^2 a_2, \ldots, \lambda_0 \lambda_1^n a_n)$$

where

$$\lambda_0 = \frac{1}{a_0}, \qquad \lambda_1 = \frac{a_0}{a_1}$$

Thus

$$x = \frac{a_0}{a_1} \sum_{i_2=0,\ldots,\ i_n=0}^{\infty} \frac{(-1)^{1+i_1}!}{(i_0+1)} \cdot \begin{pmatrix} i_1 \\ i_2 \ldots i_n \end{pmatrix} \cdot \prod_{k=2}^{n} \left(\frac{a_0^{k-1} a_k}{a_1^k} \right)^{i_k}$$

$$\equiv \sum_{i_2=0,\ldots,\ i_n=0}^{\infty} \frac{(-1)^{1+i_1}!}{(i_0+1)} \cdot \begin{pmatrix} i_1 \\ i_2 \ldots i_n \end{pmatrix} \cdot \frac{a_0^{1+i_0} \prod\limits_{k=2}^{n} a_k^{i_k}}{a_1^{1+i_1}}$$