

L. A. Tavadyan
G. A. Martoyan

Analysis of Kinetic Models of Chemical Reaction Systems

Value Approach

*Chemistry Research
and Applications*

NOVA

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OF CHEMICAL REACTION SYSTEMS.
*VALUE APPROACH***

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**ANALYSIS OF KINETIC MODELS
OF CHEMICAL REACTION SYSTEMS.
*VALUE APPROACH***

L. A. TAVADYAN AND G. A. MARTOYAN
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This publication is designed to provide accurate and authoritative information with regard to the subject matter covered herein. It is sold with the clear understanding that the Publisher is not engaged in rendering legal or any other professional services. If legal or any other expert assistance is required, the services of a competent person should be sought. **FROM A DECLARATION OF PARTICIPANTS JOINTLY ADOPTED BY A COMMITTEE OF THE AMERICAN BAR ASSOCIATION AND A COMMITTEE OF PUBLISHERS.**

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PREFACE

The problem of numerical modeling of complex chemical reactions attracts the increasing attention of researchers associated with the tendency to control efficiently chemical reactions in practical applications. The mechanism of the complex (multistep) reaction or, otherwise, its kinetic model is defined as a set of single-step individual chemical transformations.

Construction of kinetic models conforming to experimental data and having prognostic capability enables the successful control of one of the major problems of chemical kinetics of complex reactions. Meanwhile, in solving this problem the broad application of conventional analytical methods is a challenge.

Computational approaches enable to overcome the “barriers” of high complexity in chemical transformation. However, the use of numerical methods in their simplest versions does not possess an ideological content. This book is addressed just to provide a practical understanding of the calculational methods.

The book was intended and written with an objective to present new kinetic approaches, which provide insight into the mechanism of the complex chemical reactions using numerical methods.

In fact, the conceptual and valid basis for these approaches is the creation of the methodology and tools for rigorous kinetic orientation in complex chemical transformation. We believe that the solution of the above-mentioned critical problem of chemical kinetics of complex reactions lies just on this path.

Recent efforts of the authors resulted in development of a numerical method for the analysis of reaction mechanisms, based on their Hamiltonian systematization with marking out target characteristics of reactions and with the kinetic comprehension of conjugate variables. The core factor of this approach is the ability to calculate numerically the dynamics of *value* magnitudes, which characterize the systemic kinetic significances of the chemical species of a reaction and its individual steps. Such information makes it possible to realize chemically the mechanism of a complex transformation, and particularly, to carry out the purposeful selection of efficient ways to control the reactions.

Without taking account of the shape of mathematical representations, the basic point that forms the foundation of the *value* approach in the study of the reaction mechanisms, may be specified as follows: different types of matter motion, including chemical transformation, can be described by similar concepts. In this case the *value* quantities, as new universal concepts of chemical kinetics, arise from the physico-chemical and kinetic understanding of the ideas

of the classical Hamiltonian formalism for dynamic systems in describing the kinetics of multistep chemical reactions.

In the book the capabilities and distinctive features of the suggested *value* analysis method of the reaction mechanisms are discussed in detail. Besides, a short and contrastive overview of existing approaches for studying and controlling the complex reactions is presented. The structure of the book includes a wide range of problems associated with the numerical *value* to describe and study the kinetics of complex reactions, such as:

- The numerical determination of kinetic significances for the individual steps and species of a complex chemical reaction;
- The reduction of excessive kinetic reaction models; via the identification of the base(minimal) reaction mechanisms;
- The identification and analysis of reaction critical conditions under which the qualitative and quantitative characteristics of the reaction change drastically;
- The identification of priorities that have target-oriented influence on a chemical reaction via optimal control;
- The determination of the molecular design of an efficient stimulators and inhibitors of a complex reaction among a number of similar compounds on the basis of kinetic model;
- The evaluation and improvement of prognostic capability of the kinetic model of a multistep reaction.

Chain chemical reactions are the dominant objects of studies in this volume. Historically, just the chain theory mainly initiates a new philosophy for chemical reactions that is the system analysis.

Chain reactions belong to the class of chemical processes for which the kinetic laws are studied extensively. In the book selection of the reactions with the aim to demonstrate the capabilities of the *value* approach was mainly based on the scientific interests of the authors. However, at the same time the examples are provided on the use of the proposed approach to solve the key problems that are relevant to chain reactions. Among these are the identification and analysis of critical phenomena, the explosion limits in branching-chain reactions, the interpretation of the molecular structure of an efficient antioxidants, the identification of dominant steps responsible for its activity, etc.

In this volume we also considered the self-organizing systems consisting of the oscillating reactions, of which the Belousov-Zhabotinsky reaction is a well-known example. Attempt was made to demonstrate a generality of the problem on the identification of critical phenomena in branching-chain reactions and in the nonlinear reaction systems as a whole.

It is important that the *value* method of studying complex chemical reactions is easily compatible with computational methods of calculation. This emphasis is validated by the kinetic software package VALKIN described here.

The authors hope that in this volume the offered *value* method for analyzing kinetic models of multistep reactions will find followers among researchers, who are dealing with the problems of chemical kinetics, the studies of the reaction mechanisms and their control. The book also will be useful for students and graduates to extend their knowledge in this field. At the same time we appreciate to receive the reader's feedback and suggestion.

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Chapter 1

FUNDAMENTALS OF CHEMICAL CHAIN REACTION KINETICS

This chapter introduces the basic concepts of the kinetics of chain reactions, which serve as the basic tool for the value approach in the kinetics of chain processes. In the frame of simple, one- and two-centered kinetic models, all types of chain reactions are presented, such as the nonbranching, branching and degenerate-branching ones. An important characteristic of chain reaction, the chain length, is interpreted from the kinetic standpoint. For nonbranching chain reactions the chain length is equal to the ratio of the rates of the chain propagation and breaking steps. The branching chain reactions are characterized by critical (limiting) phenomena, consisting of sharp quantitative and qualitative changes in the mode of reactions, with small changes in the initial concentration of reactants, the kinetic parameters of reaction systems or their external conditions. When considering the branched chain process such as the reaction between hydrogen and oxygen, in terms of the temperature and pressure coordinates, the region of intense reaction (the auto-ignition region) is clearly distinguished from the region of slow reaction.

The difference between the kinetic behavior of conventional branching and degenerate- branching reactions is conditioned by the fact that for degenerate-branching reactions the act of branching under which the multiplication of carrier chain occurs, proceeds with the participation of a “mediator”, that is an intermediate molecular (nonradical) product.

Chain reactions were discovered by M. Bodenstein [1] in 1913 by the example of photochemical reaction of hydrogen chloride formation from molecular chlorine and hydrogen.

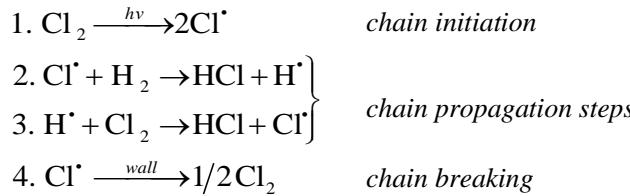
Subsequent discoveries in this field and formulation of the fundamentals of the chain reactions theory, including branching chain reactions, is linked, to a large extent, with the names of N.N. Semenov [2] and C.N. Hinshelwood [3]. So far the efforts of the scientists in this area are focused on detailed study of the chain reactions.

A number of original monographs and textbooks [3-31] are dedicated to chemical chain reactions. Here we provide a minimum of information on the kinetics of chain reactions, which is primarily intended to create the necessary basis for stating in subsequent Chapters the concept of the *value* description for the kinetics of chain reactions.

1.1. NONBRANCHING CHAIN REACTIONS

Chain reaction is defined as a transformation process of initial substances into the products through periodic alternation of elementary steps with the participation of active intermediates, mostly free radicals and/or atoms.

Hydrogen chlorination is considered as a classical reaction proceeding through the following set of elementary steps:

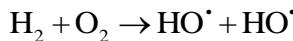


Due to higher rate constant for the step (3) as compared with the similar step (2), the concentration of Cl^\bullet atoms is considerably higher than that of H^\bullet atoms. Therefore, in the reaction mechanism it is enough to take into consideration the chain breaking occurring only with the participation of Cl^\bullet atoms.

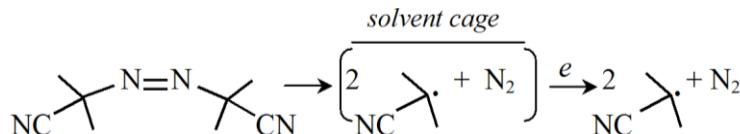
In that way a nonbranching chain reaction proceeds through three types of elementary steps: initiation (generation), propagation and breaking of the chain.

Let us consider the chain carriers: atoms and/or free radicals.

At the *chain initiation* stage the particles with an unpaired electron on the external orbital are generated from valence-saturated molecules of initial reagents or special substances - initiators. For example:



or decomposition of the initiator 2,2'-*azo-bis-iso*-butyronitrile (AIBN)



where e is the escape probability of the cyanoisopropyl radical from the *solvent cage*.

The *chain breaking* stage results in the removal of the chain carriers, e.g. step (4) in the reaction mechanism of hydrogen chlorination.

At the *chain propagation stage* another chain carriers arises as a result of reaction between the initial reagent and chain carrier. Steps (2) and (3) in the above-mentioned reaction mechanism of hydrogen and chlorine may serve as examples of such a stage.

The *chain length* is an important parameter for the chain process. Chain length is determined by the average number of the *chain links*, through which the chain process is realized. In turn the chain link represents a cyclic process, involving successive elementary steps of chain propagation, where the active species originating this sequence appears again.

Steps (2) and (3) in the chain reaction of hydrogen with chlorine cited above represent the chain link.

It is appropriate to mention here that the chain link may involve only one step of chain propagation. For example, for free radical polymerization of the vinyl monomer, $\text{CH}_2=\text{CHX}$, the chain link includes the only reaction of the growing free radical (macroradical) addition to the monomer:

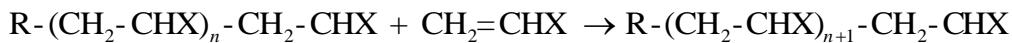


Figure 1.1 shows a diagram of a chain process.

The probabilistic theory of one-centered model for a chain process is described in [2]. Below its summary is given.

Elementary probabilistic theory for non-branching chain reactions. An active intermediate being generated in a non-branching chain reaction has two chances: (i) enter into a chain propagation reaction with a probability value α or (ii) to be lost with a probability value β , such that $\alpha + \beta = 1$.

The probability that S recycling takes place in the chain, followed by its breaking at the $(S+1)$ cycle is equal to:

$$P_S = \alpha^S \beta = \alpha^S (1-\alpha)$$

Hence the average chain length may be defined as the mathematical expectation of a random quantity S with a probability P_S :

$$\nu = \bar{S} = \frac{\sum_{S=0}^{\infty} P_S S}{\sum_{S=0}^{\infty} P_S} = \frac{\alpha}{1-\alpha} = \frac{\alpha}{\beta} \quad (1.1)$$

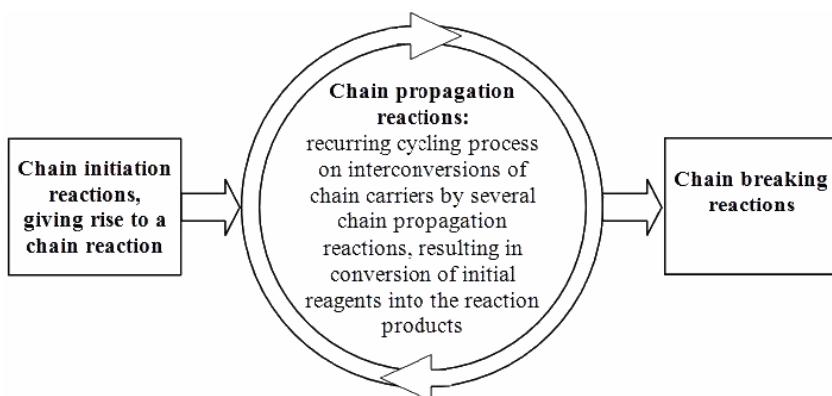


Figure 1.1. Diagram of a chemical chain process.

As applied to the chain reaction of hydrogen chlorination, we have

$$\begin{aligned}\alpha &= \frac{r_{\text{prop}}}{r_{\text{prop}} + r_t} = \frac{k_2[\text{Cl}^\cdot][\text{H}_2]}{k_2[\text{Cl}^\cdot][\text{H}_2] + k_4[\text{Cl}^\cdot]}, \\ \beta &= \frac{r_t}{r_{\text{prop}} + r_t} = \frac{k_4[\text{Cl}^\cdot]}{k_2[\text{Cl}^\cdot][\text{H}_2] + k_4[\text{Cl}^\cdot]}, \\ \nu &= \frac{k_2[\text{Cl}^\cdot][\text{H}_2]}{k_4[\text{Cl}^\cdot]} = \frac{r_{\text{prop}}}{r_t},\end{aligned}\quad (1.2)$$

where r_{prop} and r_t represent the chain propagation and breaking reaction rates, respectively, and $[\cdot]$ denotes the concentration of the species.

Time dependence for the concentration of active intermediates and the rate of a non-branching chain reaction. The accumulation rate for active intermediates of a chain reaction is described by the following expression:

$$\frac{dn}{dt} = r_i^0 - gn \text{ and, accordingly, } n = \frac{r_i^0}{g}[1 - \exp(-gt)] \quad (1.3)$$

with the initial condition $n(t_0) = 0$.

Here r_i^0 is the initiation rate of active intermediates, n is their concentration, g is the specific rate for the chain breaking (chain breaking rate per unit concentration of active intermediates).

The initial reagent is consumed in each chain link. Therefore for long-chain chemical reactions the reaction rate (r) is determined by the chain propagation rate

$$r = an = \frac{ar_i^0}{g}[1 - \exp(-gt)], \quad (1.4)$$

where $a = k_{\text{prop}}[\text{B}]$, $[\text{B}]$ is concentration of the initial reagent, k_{prop} is the rate constant for the rate-limiting stage (the relatively slow one from the consecutive stages) of chain propagation.

According to (1.4), after a time interval

$$t > 3\tau_{\text{ch}} = 3g^{-1}, \quad (1.5)$$

a reaction regime is established for which the chain reaction rate will be equal to:

$$r = \frac{ar_i^0}{g}, \quad (1.6)$$

with an average time for chain development τ_{ch} , equal to realization of the chain process, starting from the chain carrier (an active intermediate) generation till its termination.

The equation (1.6) describes the rate of non-branching chain reaction, which is accurate to within 5% already at $t = 3g^{-1}$.

According to (1.2) average length of the chain is

$$v = \frac{an}{gn} = \frac{a}{g} \quad (1.7)$$

Then the fundamental relationship for a non-branching chain reaction may be derived from (1.6) and (1.7):

$$r = r_i^0 v. \quad (1.8)$$

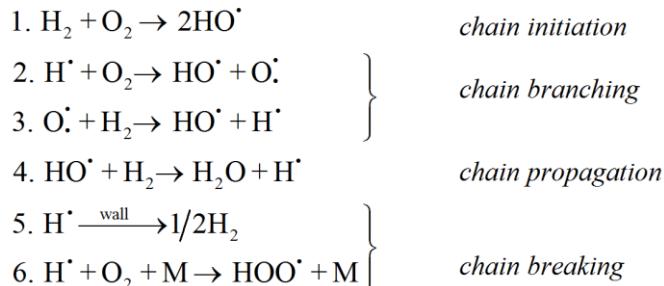
In conformity with this equation one can control the rate of a chain reaction, namely, accelerate it by increasing the chain initiation rate or slow it down by raising the probability of chain breaking (thus reducing chain length).

Comparing (1.2) and (1.8) it may be easily demonstrated that at the steady-state regime of non-branching chain reaction $r_i^0 = r_t$.

1.2. BRANCHING CHAIN REACTIONS

Reproduction of the chain carriers does not occur in the propagation stage of the non-branching chain reactions discussed above. If reproduction of chain carriers occurs in the propagation stage then a fundamentally new effect is available. In this case a newly generated chain carriers results in several chains [2,3] due to the branching process.

The reaction between hydrogen and oxygen is a classical example of a branching chain reaction [2-8]. Its basic kinetic features may be understood within the framework of the following simple mechanism:



where M is an arbitrary particle.

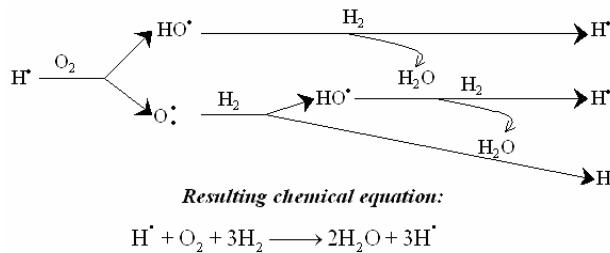
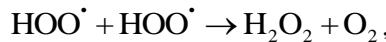


Figure 1.2. Diagram of branching process for the reaction between hydrogen and oxygen.

It is assumed that the relatively less active free radical $\text{HOO}\cdot$ does not participate in the chain reaction development, and either undergoes a recombination reaction:



or is deactivated on the inner surface of the reaction vessel.

As schematically illustrated in Figure 1.2 a single branching act results in the reproduction of the chain carriers: finally instead of one chain carrier (hydrogen atom) three hydrogen atoms are formed.

Critical (extreme) phenomena are the specific features of the branching chain reactions: namely, qualitative transfer from a slow reaction regime to an intensive (self-accelerated) one at minor changes in concentration of the initial reagents, kinetic parameters of the reaction system or ambient conditions. The region of the intensive reaction in the coordinates of temperature *vs.* pressure forms the so-called ignition peninsula [2,3] demonstrated in Figure 1.3.

Elementary probabilistic theory of branching chain reactions. If branching occurs in a chain reaction then expression (1.1) for the average chain length includes the branching probability (δ), which acts to decrease the chain breaking probability

$$v_b = \frac{\alpha}{\beta - \delta} \approx \frac{v}{1 - v\delta}.$$

In this case the reaction rate is

$$r_b = \frac{r_i^0 v}{1 - v\delta}. \quad (1.9)$$

Expression (1.9) predicts the aforementioned specific features of the branching chain reactions: the existence of two qualitatively different regimes of a chemical process. The reaction changes from a slow regime ($\beta > \delta$) to that of a continuous increase in chain

number ($\beta < \delta$). $\beta = \delta$ is the condition determining the limit (boundary) of the two reaction regimes.

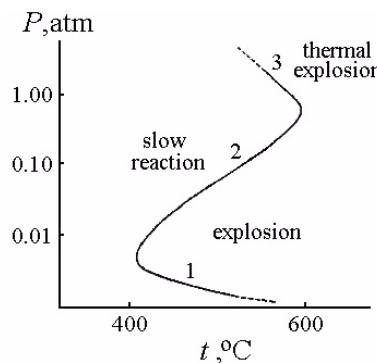


Figure 1.3. Explosion limits (1-3) for the stoichiometric mixture of H_2 and O_2 depending on initial temperature and pressure (schematic illustration).

Time dependence for the concentration of chain carriers and the rate of a branching chain reaction. The rate of chain carrier accumulation for branching chain reaction is

$$\frac{dn}{dt} = r_i^0 + (f - g)n, \quad (1.10)$$

where f is the specific rate of branching (per unit concentration of chain carriers).

The expression (1.10) is true if one-centered branching chain reaction is considered. Such an approach describes adequately the behavior of the branching chain reaction provided that the *partial steady-state conditions* are valid, i.e. assuming steady-state concentration of active intermediates, except for one chain carrier of significantly higher concentration. In case of branching chain reaction between hydrogen and oxygen one can assume that

$$d[\text{O}]/dt = 0, \quad d[\text{HO}^\cdot]/dt = 0, \text{ and } d[\text{H}]/dt \neq 0.$$

In the approximation of time-constant r_i^0 , g , f and $n(t_0) = 0$

$$n = \frac{r_i^0}{\varphi} [\exp(\varphi t) - 1]$$

and, accordingly, the reaction rate is

$$r = \frac{ar_i^0}{\varphi} [\exp(\varphi t) - 1] \quad (1.11)$$

where a describes the specific rate of interaction between the initial reagent and the chain carrier: $a = k[B]$, k is the effective rate constant, $[B]$ is the concentration of the initial reagent; $\varphi = f - g$ is a factor of self-acceleration being a key parameter for a branching chain reaction. It is the sign of φ that determines the reaction regime as follows (see Figure 1.4).

$$\text{Slow regime: } (\varphi < 0) \quad r = \frac{ar_i^0}{|\varphi|}. \quad (1.12)$$

As shown in Figure 1.4 a decelerating growth in the values of n and r takes place, tending to the quasistationary magnitude, under the conditions of insignificant consumption of initial reagents

$$\text{Self-accelerated regime: } (\varphi > 0) \quad r = \frac{ar_i^0}{\varphi} \exp(\varphi t). \quad (1.13)$$

Equations (1.12) and (1.13) are written down assuming that the reaction time, according to (1.11), is much greater than $3/\varphi$. At $t = 3/\varphi$ the reaction rate differs a mere 5% from the values given by equations (1.12) and (1.13).

The condition $\varphi = 0$ describes the boundary for critical transition from one reaction regime to another. In this case $r = ar_i^0 t$.

1.3. DEGENERATE BRANCHING CHAIN REACTIONS

A very important class of autoxidation of organic compounds belongs to this type of reactions (cf. [2,8,9,32-37]). As with the branching chain reactions, these reactions also are characterized by self-acceleration due to autoinitiation. In the course of the reaction a molecular compound is formed, which generates the chain carriers more intensively as compared with the initial compounds. According to N.N. Semenov, who created the fundamentals of the theory [2], these reactions are similar to the branching chain ones, while occurring more slowly and in another time scale. These reactions are considered as processes with degenerate chain branching.

In these reactions, chain branching represents the stage of chain- carrier generation solely with the participation of molecular product(s) formed at the chain propagation stage. Schematically such a process may be represented as follows



where A, P, C denote the initial, intermediate nonradical and stable end molecular products, respectively, θ is the time required for the generation of a chain carrier (n) from the intermediate compound P.

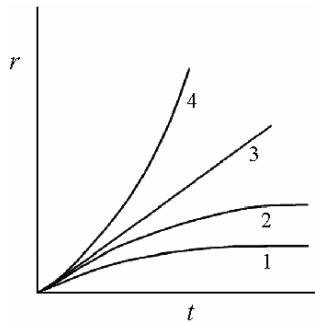


Figure 1.4. Time dependence for chain reaction rate (consumption of initial reagents is not taken into account): ($f = 0$) (1) - no branching; ($\phi < 0$) (2); ($\phi = 0$) (3); ($\phi > 0$) (4).

The value of θ determines the branching type:

$\theta > \tau_{ch}$ - degenerate chain branching;

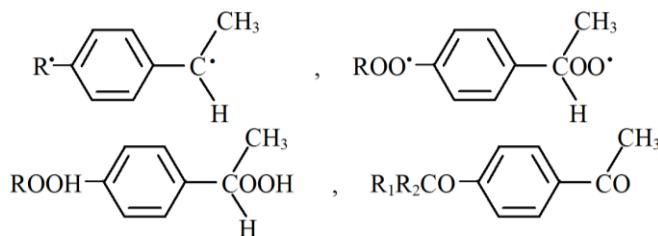
$\theta < \tau_{ch}$ - chain branching.

Liquid phase oxidation of hydrocarbons (RH) [9,32-37] may serve as an example of a degenerate branching chain reaction. At relatively low temperatures (50-110°C) and in the presence of catalysts, the mechanism of this process may be described by the following sequence of reactions:

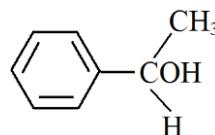
1. $2RH + O_2 \rightarrow 2R\cdot + H_2O_2$ *chain initiation*
 2. $R\cdot + O_2 \rightarrow ROO\cdot$
 3. $ROO\cdot + RH \rightarrow ROOH + R\cdot$
 - 4,5. $ROOH \xrightarrow{cat.} ROO\cdot$ *degenerate chain branching*
 6. $ROO\cdot \xrightarrow{cat.} R_1R_2CO + H_2O$ *nonradical products*
- \downarrow

where *cat.* indicates stages that occur with the participation of a catalyst.

In case of ethylbenzene ($\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$) the intermediate molecular compounds and free radicals are characterized by the following structures



Nonradical reaction products apart from hydroperoxide most likely represent acetophenon (see above) and methylphenylcarbinol.



According to the reaction scheme shown above, the hydroperoxide formed in the chain propagation stage with the participation of an initial organic substrate is responsible for the degenerate chain branching.

For a degenerate branching chain reaction, the rate of chain carrier and the intermediate product P accumulation is expressed by the following equations:

$$\begin{aligned}\frac{dn}{dt} &= r_i^0 + fP - gn, \\ \frac{dP}{dt} &= an - cP,\end{aligned}\tag{1.15}$$

where a and c represent kinetic factors for chain propagation and transformation of P , respectively; f is the kinetic factor for chain carrier formation from the intermediate nonradical product P .

For degenerate branching chain reactions, in contrast to branching ones, the steady-state concentration approach is often valid for concentrations of all active intermediates: $dn/dt = 0$ at $t > \tau_{ch}$. Taking into account negligible consumption of the initial reagent one can derive from equations (1.15), respectively

$$\begin{aligned}P &= \frac{r_i^0 v}{\varphi} [\exp(\varphi t) - 1] \\ n &= \frac{r_i^0 + fP}{g}\end{aligned}\tag{1.16}$$

where $(v = \alpha/g)$ is the chain length, and $\varphi = (fa/g - c)$ is the self-acceleration factor.

The consumption rate for the initial reagent A also may be determined easily, provided that $fP \gg r_i^0$, that fits to a degenerate branching chain process

$$r_A = an \approx \frac{afP}{g} = \frac{fv^2 r_i^0}{\varphi} [\exp(\varphi t) - 1] \quad (1.17)$$

The kinetic factors for the above-mentioned hydrocarbon oxidation scheme are as follows:

$$a = k_3[\text{RH}], g = k_6[\text{cat}], f = k_4[\text{cat}], c = (k_4 + k_5)[\text{cat}].$$

More detailed information related to the kinetic equations of the degenerate branching chain reactions for different mechanisms of generation and termination of chain carriers may be found in the monograph [9].

It follows from expressions (1.16) and (1.17) that two reaction regimes are typical, both for the degenerate branching and non-branching chain reactions:

$$\text{Slow regime } (\varphi < 0), P = \frac{r_i^0 v}{|\varphi|}, r = \frac{fv^2 r_i^0}{|\varphi|}. \quad (1.18)$$

$$\text{Self-accelerated regime } (\varphi > 0), r = \frac{fv^2 r_i^0}{\varphi} \exp(\varphi t). \quad (1.19)$$

Equations (1.18) and (1.19) are valid for $t > 3\varphi$.

Here, changing from one regime to another is also characterized by the critical phenomena [2, 8, 37]. The critical state of a reaction system corresponds to the following condition:

$$\varphi = 0. \quad (1.20)$$

For the degenerate branching chain reactions the critical phenomena are expressed more distinctly at better fulfillment of the following inequalities

$$v \gg 1, fP \gg r_i^0.$$

In the degenerate branching chain reactions, as distinct from the branching chain ones, the reason of critical phenomena lies not only in the change of the regime for chain carriers accumulation, but also in the same for the intermediate nonradical product P , that is in this case the intermediate nonradical products play an active role. It is necessary to remind that the value of φ , which determines the regime of the process development, is the difference between the rates of branching and termination of chain carriers (per unit concentration of chain carrier). A somewhat different situation is for the degenerate branching reactions. Here, the sign of φ is determined by the difference between the rates of intermediate nonradical product formation (responsible for the degenerate branching of the chains) in the chain propagation (faP/g) stage and its consumption (cP).

CONCLUSION

As follows from a brief review of the fundamentals on the kinetics of chain reactions, an elegant one-centered model of the process, which was offered at the beginning of the development of the chain reaction theory, provides a phenomenological description. Initiation and inhibition of reactions by small additions of compounds, critical phenomena, etc. may serve as examples. However, it should be noted that modeling a chain reaction is usually complicated, if the one-centered approximation is not justified and in the cases when consumption of initial compounds should be taken into account, or when the intermediates are participating in the chain process, in other words if one has to deal with chain processes of a more complicated nature. So the efforts aimed at developing the special theoretical approaches that are thought to help for a better orientation in a complex chain chemical process are justified, in particular, under the conditions of multi-centered, and consequently multi-routed occurrence.

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Chapter 2

KINETIC SIGNIFICANCE OF STEPS IN COMPLEX CHEMICAL TRANSFORMATION

This chapter is aimed to show the importance of determining the kinetic significance of individual chemical steps to illuminate the essence of the reaction mechanism. A short overview is presented and a critical analysis is given for the existing methods that assess the significance of chemical species and individual steps in the kinetic models of chemical reaction systems.

For kinetic studies of multistep chemical reactions, one of the key stages in the general modeling strategy is to identify the role of individual steps and the chemical species of reactions. Three approaches are considered to identify the significance of individual kinetic steps: a) analytical, b) Horiuti's "pathway" theory, and c) the parametric sensitivity analysis method. The most advanced method is the parametric sensitivity analysis. This is due to its successful combination with numerical methods in studies of reaction mechanisms. Sensitivity analysis mainly comes down to the determination of the responses (sensitivities) of some output parameters (frequently, the concentration of species or the characteristics of the reaction functionally dependent on them), to small changes in the rate constants of individual steps. When using sensitivity analysis, however, there are problems associated with the quantitative interpretation of sensitivity parameters. For this reason, to a large extent, while reducing the excess reaction mechanisms by identifying the non-essential individual steps, sensitivity analysis is often used in conjunction with other numerical methods.

Kinetic study of a complex chemical reaction ultimately comes to the construction of a mathematical model for it. In this case, to solve each specific task on modeling a chemical reaction, as a rule a researcher selects the following strategy (see, for example [1-10]):

1. Definition of the problem, which mainly comes to answer the question: what is the purpose of the kinetic model? (describing experimental data, understanding the chemical nature of the reaction, revealing the nature of new chemical phenomena, obtaining the prognostic model for successfully controlling and so on).
2. Construction of a hypothesis concerning the kinetic model of the reaction. Mostly it means a definition of a sequence of steps, as the species for the kinetic model of the reaction. Here the possibility of using the computer approaches to construct the primary hypothesis about the reaction mechanism also should be taken into consideration. This question will be discussed in Chapter 3.

3. Construction of the reaction kinetic scheme (mechanism), which includes, in addition to the elementary reactions, the data on the rate constants for these reactions.
4. Compiling a mathematical model for the reaction, which represents a system of differential equations. This system may be a result of applying the mass action law

$$\frac{dc_i}{dt} = f_i(\mathbf{c}, \mathbf{k}), \quad i = 1, 2, \dots, m, \quad \mathbf{c}(t_0) = \mathbf{c}^0, \quad (2.1)$$

where c_i is the concentration of the i -th species of the reaction; \mathbf{k} and \mathbf{c} are the vectors of rate constants for individual steps and the concentrations of species in a complex reaction, \mathbf{c}^0 are the initial concentrations. Here it should be mentioned that in (2.1) the deterministic models are meant. Stochastic (probabilistic-statistical) models are also known that are provided, for example, in [7,11].

5. Integration of the system of equations (2.1).
6. Verification of the model adequacy with the experimental results.
7. Model correction if necessary.
8. Analysis of the kinetic model behavior, model update, and the planning of experiments aimed at updating the model.
9. Reduction of the kinetic model leading to the decrease in the number of the individual steps and species.
10. Forecasting the behavior of the chemical reaction, defining the limits for adequate functioning of the kinetic model and controlling the chemical reaction.

In the above, the stage 8 is the key one for the mathematical modeling of the complex chemical reaction. It should be emphasized that this stage is in harmony with the overall context of procedures at mathematical modeling of chemical reactions. In this way M.J. Pilling [4] considers the process of constructing, examining and reducing kinetic models for the chemical reactions as a comprehensive whole. Stage 8 enables to perform a rigorous analysis of the mathematic model's behaviour and its testing from the chemical point of view. Proper selection of the final kinetic model of the reaction, successful planning of new experiments aimed at updating the model strongly depend on the above. Finally, additional opportunities arise for the construction of kinetic models with relatively higher forecasting potential.

Note that *when analyzing the kinetic models of reactions it is crucial to identify the kinetic significance of distinct steps and the chemical species of the reaction*. Below we will try to motivate the urgency of such problem definition.

2.1. IDENTIFICATION OF THE KINETIC SIGNIFICANCE FOR INDIVIDUAL STEPS AS AN OUTSTANDING STAGE IN THE STUDY OF MODELS OF CHEMICAL REACTION SYSTEMS

It is well-known that a complex chemical transformation occurs due to the realization of a great number of elementary reactions. As mentioned earlier, it is thought to be the most

important the fact that the complex chemical reaction should be considered as a reaction system. Here, individual steps are not independent, but participate in the process being interconnected, because of the mutual influence on the concentration of the initial and intermediate compounds taking part in these steps.

It follows from such comprehension of the main point of complex chain reaction that it is an unavoidable situation when it becomes clear, what chemical transformations can occur in the interaction between the species of the reaction system (and with what probability) and whether it is difficult to forecast their impact on the complex chemical transformation as a whole. For illustration let us refer to the well-studied example of the chain reaction between molecular hydrogen and oxygen (see Chapter 1). In this case one can clearly conceive a chemism of the reaction having available its kinetic model. However, identification of the kinetic significance of steps in the behavior of a chain reaction requires performing a special system analysis.

So, it becomes clear that when using complex kinetic models for reactions (which is often unavoidable), a chemist-researcher loses to a great extent his or her basic “tool”: the structural approach. That is, it is difficult to understand how in the chemism of the reaction, the molecular structure of the initial and intermediate substances determine the time-dependent changes in the rate of chemical reactions and the composition of products.

Not the least of the factors is that in such cases it becomes considerably less productive using the “ping-pong” kinetics, being one of the effective means for revealing the complex reaction mechanism. The “ping-pong” kinetics implies alternatively performing the following research steps: on the basis of kinetic observations a reaction mechanism is suggested, which should be further verified experimentally (see Figure 2.1). This procedure may be continued repeatedly, e.g. up to attaining an acceptable adequacy between the kinetic model and the experimental data. Lack of information about the role of different chemical transformations and species of the reaction system or its total absence constrict considerably the ability to interpret experimental data and, consequently, to plan the desirable “key” experiments aimed at updating the reaction mechanism.

A similar situation may arise at developing the ways for purposefully affecting upon a chemical reaction by means of active additives, promoters, inhibitors, catalysts, and others, which are participating in the reaction steps. This question is covered in more details in Chapter 4.

The above convince us that identification of the kinetic significance of individual steps and species in a chemical reaction is the fundamental issue for the kinetics of complex chemical reactions.

Thus, it may be concluded that determining the role of individual steps is associated with solving the following, more or less different important problems of the chemical kinetics for revealing the:

- reaction mechanism and nature of chemical transformations;
- influence of the electronic structure of reaction system species on the main kinetic laws of a chemical reaction;
- ways of purposefully affecting a chemical reaction.

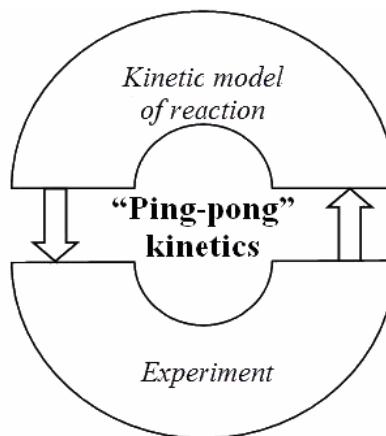


Figure 2.1. Schematic pattern of procedures in the “ping-pong” kinetics.

It should be emphasized again that *identification of the kinetic significance of steps in a reaction system provides the successful coupling of theory and experiment in the kinetics of chemical reactions, aimed at solution of objective-oriented problems of chemistry.*

2.2. MATHEMATICAL METHODS FOR IDENTIFICATION OF KINETIC SIGNIFICANCE OF INDIVIDUAL STEPS IN CHEMICAL REACTION SYSTEMS

In this section the more formalized methods on determining the role of individual steps in complex chemical reactions are briefly described.

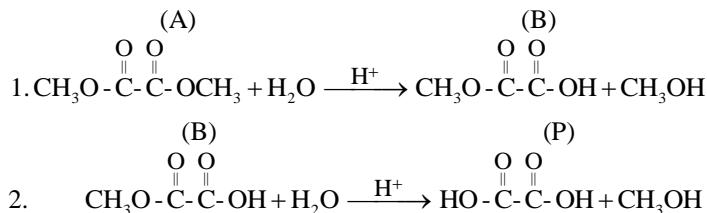
2.2.1. Analytical Description of Kinetic Regularities of Chemical Reactions

Analytical description of the chemical reaction progress with time, within the framework of a specific model, enables mostly to identify the kinetic significance of the individual steps, as a dependence of the rates or concentrations of the reaction species on the rate constants of the contributing steps and the measured values. It should be noted that the exact knowledge of the numerical values of rate constants for individual steps is not always required. Often it is enough to have information on their limiting and/or relative values.

To be illustrative let us refer to a simple consecutive reaction



For example, hydrolysis of esters of dicarboxylic acids belongs to such reactions. Thus, dimethyl ester of the oxalic acid is hydrolyzed through two steps



The analytical expression for the time-dependency of the concentration of the intermediate compound B is

$$[\text{B}] = [\text{A}]_0 \frac{k_1}{k_2 - k_1} [\exp(-k_1 t) - \exp(-k_2 t)]. \quad (2.2)$$

where $[\text{A}]_0$ is the initial concentration of the substance A.

It follows from (2.2) that the concentration of B, reaches its maximum value $[\text{B}]^{\text{max}}$ at the time

$$t_{\text{B}^{\text{max}}} = \frac{\ln(k_2 / k_1)}{k_2 - k_1} = \frac{\ln q}{k_1(q-1)}, \quad (2.3)$$

where

$$[\text{B}]^{\text{max}} = [\text{A}]_0 q^{\frac{q}{1-q}}, \quad (2.4)$$

and $q = k_2 / k_1$.

The role of the consecutive reaction steps in the kinetics of intermediate product accumulation becomes apparent from the expression (2.4). In particular, it follows from (2.3) and (2.4) that the higher is the value of q , the lower is the concentration of the intermediate product B and this concentration is achieved earlier (Figure 2.2).

Obviously, the “analytical” approach may be inconsistent when using a sufficiently complicated (multistep) model for a chemical reaction. Therefore, the need of analytical solutions motivates a researcher to make different simplifications of the original kinetic model. In the majority of cases such a procedure is quite reasonable. Nevertheless, it should be borne firmly in mind that such a “compromise” to a certain extent may move away the real process from its mathematical model. It is generally known that a complex chemical reaction system is not a consequence of ordinary complication of a more simplified model. It may be endowed with an essentially new objective intention that is missing in the simplified model.

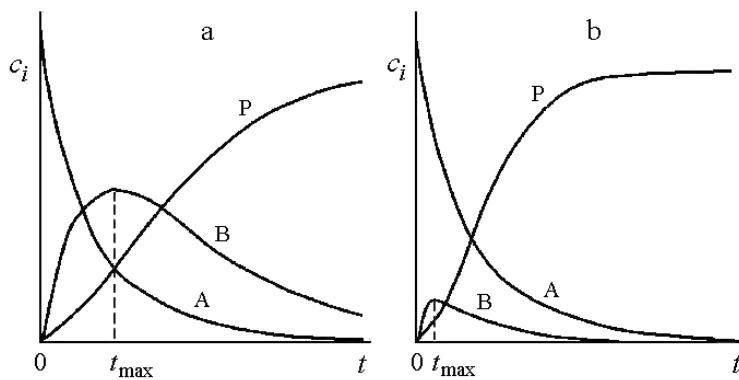


Figure 2.2. Kinetic curves of species in the consecutive reaction $A \rightarrow B \rightarrow P$. The value of $q = k_2/k_1$ is greater in the case (b) as compared to the case (a).

Researchers try to overcome this difficulty in a certain degree by composing a “mosaic” picture of chemical transformation. This implies the obtaining of so-called “cuts” of kinetic hypersurface, in the parameter space describable analytically. In fact, this procedure represents usage of the decomposition method: splitting the original model into a number of autonomous mathematically analyzable subsystems of less complexity. Then the overall kinetic pattern of chemical transformation is compiled, based on considered “cuts” - elements of mosaic. Here finding the key “cuts” and the adequate synthesis (composing) of the overall picture of chemical transformation is of fundamental importance. Obviously the efficiency of applying this approach depends substantially on the test subject and the set goals. Also it is evident that the approach in question may not be considered as comprehensive. We will revert to this question in connection with the quantitative interpretation of the inhibited chain reaction mechanism on the oxidation of organic compounds (see Chapter 7).

For example, W. Gardiner [3] when evaluating the capabilities of this method in connection with the studies of the complex nature of combustion reactions, states: “For the major part of the period of combustion science development, its complexity could be presented just as a mosaic picture, reminding to a great extent a situation, when someone is trying to understand the nature of a large country through a set of instant photos of its individual parts”.

Making this quotation we rather strive to focus attention on the ability of unbiased study of the chemical reaction by means of compiling a “mosaic” pattern of its model and do not call the scientists in this field to reject this effective approach.

Despite the mentioned limitations the analytical method is also attractive because it allows the revealing of characteristic reaction parameters as well (within the limits of sufficient simplicity of the initial kinetic model). The matter is that frequently, the behavior of a dynamic system may be described more completely via characteristic parameters, representing certain proportions between rate constants of individual steps and experimentally measurable concentrations of species of the reaction system. The fact of special importance is that these values frequently lead to new concepts in chemical kinetics. For the consecutive reaction discussed above, the parameter q serves as such a characteristic one. In addressing chain processes, the chain length, the self-acceleration factor, etc. serve as such parameters (see Chapters 1 and 5).

At the same time it is necessary to overcome temptation to describe the behavior of a reaction system by means of characteristic parameters, in all cases. Moreover, instinctively it seems to be apparent that for rather complicated reaction systems the number of such parameters will be too large, even though they were identifiable.

Nevertheless, the approaches [12,13] are worthy of notice, as in some cases they enable successfully to overcome the challenges arising at choosing a complicated primary kinetic model of a chemical reaction. These researchers offer to combine the methods of numerical modeling with the identification of characteristic parameters of a multistep chemical reaction.

At the same time it seems to be attractive the viewpoint that numerical analysis of kinetic models of chemical reaction systems, defying analytical solutions, does not lie on the path of “mechanical” application of the analytical method. It seems here that more flexible and universal approaches are needed, which will be exemplified below.

2.2.2. “Pathway” Theory

Horiuti's theory [14,15] is one of the harmonious theories for complex chemical reactions. The key concept of this theory is the idea of *reaction pathways* under steady-state conditions. This provides an opportunity to describe the steady-state behavior of the concentration of intermediate species (z_i), i.e.

$$dz_i/dt = 0 . \quad (2.5)$$

To meet condition (2.5) it is necessary that the life-time of each intermediate species is considerably smaller than the reaction-time.

A detailed description of the pathway theory's basics is given in [14-21]. Here we describe briefly only some results. Let us get to know the fundamentals of this theory.

The reaction pathway specifies one of the paths of a steady-state chemical transformation and represents a set of individual steps with corresponding stoichiometric numbers, the sum of which (the resulting chemical equation) does not contain active intermediates. At the same time a certain direction of a reaction may be realized by several pathways.

For example, the catalytic reaction of isotope exchange between hydrogen and deuterium proceeds through three (I-III) reaction paths

	I	II	III	$N = I, II, III$
1. $H_2 + 2Z = 2HZ$	1	0	1	
2. $D_2 + 2Z = 2DZ$	1	0	-1	
3. $HZ + DZ = HD + 2Z$	2	0	1	
4. $HZ + D_2 = HD + DZ$	0	1	2	
5. $DZ + H_2 = HD + HZ$	0	1	0	
$\sigma_s^{(N)}, s = 1, 2, \dots, 5$				

Overall equation: $H_2 + D_2 = 2HD$

where $\sigma_s^{(N)}$ is the stoichiometric number of a step (s) in the N -th pathway; Z is an active center of the catalyst surface.

Totality of linearly independent pathways describing certain chemical transformation is identified as the basis of pathways. The maximum possible number of pathways in the basis is defined by the equality $N = N_s - N_i$, where N_s is the number of steps in the reaction mechanism under study; N_i is the number of independent intermediates that are not inter-bounded by additional conditions.

The reaction rate via the pathway is defined as the number of runs on this path per unit time per unit reaction volume.

The accumulation rate (r_{A_j}) of a certain reaction species (A_j) is connected with the reaction rates (r^N) upon the pathways of the chosen basis, according to

$$r_{A_j} = \sum_{N'} \mu'_j r^{(N')} - \sum_{N''} \mu''_j r^{(N'')} , \quad j = 1, 2, \dots, N_s - N_i , \quad (2.6)$$

where N' and N'' match the pathways by which the substance A_j is formed and consumed, respectively; μ_j is the stoichiometric factor for A_j .

At the same time the theory leads to the relation

$$r_s - r_{-s} = \sum_N \sigma_s^{(N)} r^N , \quad (2.7)$$

where r_s , r_{-s} are the rates of individual steps (s), ($-s$) for the forward and reverse directions of the reaction.

Let us address now the issue of identifying the kinetic significance of individual steps. It is easy to see that according to equation (2.7) the rate of each reverse reaction may be estimated from experimentally measured data on the rates of reaction paths. Hence, the role of (s , $-s$) steps is revealed. It should be mentioned that in the framework of pathway theory, M.I. Temkin [18] offers a method to derive the kinetic equations. This is when the rate on reaction path, and further according to (2.6) the rate of multistep reaction, is expressed through the rate constants of individual steps and characteristics, and more often concentrations of the initial substances, determined in kinetic experiments. In the final kinetic model the dependency on the rate constants of steps specifies their kinetic participation in the total chemical process [17].

Another highly remarkable feature of the pathway theory is the opportunity to deduce a final equation for the chemical transformation. At that the effective stoichiometric factors (m) of initial substances (A) and end-products (B) in the final equation of chemical transformation are expressed *via* reaction rates by paths, as

$$\sum_i m_i^A A_i = \sum_j m_j^B B_j . \quad (2.8)$$

Effective stoichiometric factors in (2.8) characterize the selectivity of a chemical reaction (see Chapter 4).

Undoubtedly the pathway approach is strictly formalized, being at the same time an efficient tool in describing the steady-state laws of chemical reactions. This theory enables to define easily the kinetic equations for the rate and selectivity of chemical processes and moreover, to express the rates of the reversible steps through the measured rates for stable reaction species. Horiuti's theory quite fairly found wide-spread use in interpreting the kinetic laws of catalytic reactions [14-21]. Meanwhile, its possibilities are seriously restricted because of the necessity to maintain a steady-state reaction mode. Nevertheless, note that some principles of the pathway theory may be extended on non-stationary regularities of chemical transformations [17].

2.2.3. Sensitivity Analysis Method

When estimating the kinetic significance of individual steps of complex reaction mechanisms today, the greatest progress is achieved by using the *method of analysis of parametric sensitivities* [3,7,22-58]. Obviously this is associated with its successful combination with numerical methods in the study of kinetic models. The sensitivity analysis method allows to interpret more intelligently the numerical data, while modeling chemical reaction systems.

The sensitivity analysis method was employed successfully for studying the mechanisms of a great number of complex chemical transformations, such as reactions on combustion [33-36], pyrolysis [37,38], the self-oscillation reaction of Belousov-Zhabotinsky [39,40], atmospheric chemistry [41-44], as well as in many other fields of natural science, such as: physics, economy, sociology, population science, etc. [7,45,46].

The main point of the method consists in determining the kinetic trajectory for responses of some reaction output parameter on the variation of rate constants of individual steps. The output parameter frequently implies the concentration of species of the reaction system or the reaction parameters for which the function type for the species concentration is known. Conceptually, via this procedure kinetic "presence" of an individual step in the reaction system is identified.

The differential (local) sensitivity for steps is written as follows:

$$S_{ij}(t) = \left(\frac{\partial c_i}{\partial k_j} \right)_t \text{ or } S_{ij}(t) = \left(\frac{\partial F_i}{\partial k_j} \right)_t, \quad (2.9)$$

where c_i is the concentration of the i -th species, k_j is the rate constant of the j -th individual step, F is the reaction output parameter, e.g. the function fitting experimental data.

Frequently the use of a normalized sensitivity coefficient, representing a dimensionless quantity

$$NS_{ij}^F(t) = (k_j/F_i) \partial F_i / \partial k_j = \partial \ln F_i / \partial \ln k_j \quad (2.10)$$

is more suitable.

Now let us address the question of calculating the sensitivity parameters.

Differentiating the kinetic equation (2.1) by k_j and taking into account (2.9) we find

$$\frac{dS_{ij}}{dt} = \frac{\partial f_i}{\partial k_j} + \frac{\partial f_i}{\partial c_i} S_{ij}, \quad i = 1, 2, \dots, m, \quad j = 1, 2, \dots, n, \quad (2.11)$$

where n is the number of individual steps, m is the number of initial and intermediate species in a multistep chemical reaction.

The combined integration of equations (2.1) and (2.11) enables to determine the time profiles of the sensitivity S_{ij} by the rate constant of an individual step j . If necessary to calculate the influence of change in rate constants of other steps, the system of equations (2.1) is integrated jointly with the corresponding system of sensitivity differential equations like (2.11).

Thus, the kinetic trajectories of sensitivities for concentration of reaction species (c_i) may be determined by the rate constants of all the steps. For this, as we have made sure, the equation system needs to be solved with the number of equations equal to the number of individual steps n ; where each of these equations, in turn, includes $2m$ differential equations.

A number of other methods that facilitate the calculation of differential sensitivities is described in the literature. Methods to calculate the local sensitivities are mainly as follows:

- “direct” method for the calculation of sensitivity dynamics based on the combined solution of differential equations (2.1) and (2.11);
- the Green’s function method [47,48];
- the method of polynomial approximation developed by Hwang [49,50]. Using this method the system of differential equations is transformed to that of algebraic equations, which facilitates considerably the problem of determining local sensitivities.

The sensitivity analysis method was realized in a number of softwares [7], such as KINAL, KINALC (T. Turanyi), CHEMKIN-II (R.J. Kee and F.M. Rupley), CHEMKIN-III Collection (R.J. Kee and co-authors).

The interval method or the so-called “brute force” method [3] also deserves attention. A specific feature of this method consists in calculating the ratio: response ($\Delta\eta_i$) of a complex chemical process at time t_f to the change in the value of the rate constant of individual steps within some interval (Δk_j) at time $t < t_f$

$$S_{ij}^\Delta = \Delta\eta_i^{(t_f)} / \Delta k_j^{(t)}.$$

More often a variation in the values of k_j is done at time zero, hence, inevitably one has to face the challenge of finding the interval sensitivities throughout the process. Attempts to carry out such “tests” on the kinetic participation of reaction steps throughout the process require an excessive expenditure of time. It is not difficult to see that the “brute force” method is much slower and less accurate than the more experienced sensitivity analysis methods.

Thus, the advantages of the sensitivity analysis method are obvious. Meanwhile, its practical use highlights a number of problems, namely:

1. Main difficulties arise when interpreting the spectrum of step sensitivities quantitatively. The problem remains also if relevant information on the values of the rate constants of individual steps is available (see Chapter 3). To resolve this not-at-all-easy task one needs to resort to intuitive assumptions and special mathematical methods. The basic ones will be thoroughly set out further [28,51,52] in connection with the problem on reducing the models of multistep reactions (Chapter 3).

The basic reason of difficulties that arise at conceiving the sensitivity kinetic trajectories is due to the fact that the sensitivity parameters specify the kinetic significance not strictly quantitatively, but for the most part qualitatively. The matter is that sensitivities of output parameters of a complex reaction, with respect to change in the values of rate constants of individual steps, characterize the influence of the rate for this step only indirectly and, consequently, its kinetic participation in the overall process. The rate of the j -th step (r_j) is equal to the product of the reaction rate constant and the concentrations of species participating in this step. So, for the bimolecular reaction $r_j = k_j c_k c_l$. It is reasonable that even if one of the individual step's species is an intermediate one, e.g. c_l , then change in k_j as a result of evolutional impact on the reaction system, may result integrally in a change of the concentration value c_l . In some cases this circumstance results in the so-called problem of "zero sensitivity". For example, if a zero value of the sensitivity does not permit to eliminate the appropriate reaction step from the kinetic scheme. In this case usually additional analysis of step rates with low sensitivity is performed [3].

The simplest mechanism on the inhibited oxidation of organic compounds (see Chapter 7) may serve as an illustrative example demonstrating such a result. Thus, a sensitivity of the induction period to the value of the rate constant of the inhibition step may be zero. However, in no way this means that the mentioned reaction is not essential. The matter is that a variation in the reaction rate constant leads to a reverse change in the concentrations of chain carriers, peroxy radicals (ROO^\bullet), but the rate of the inhibition step (r_{In}) remains constant.

$$r_{\text{In}} = \uparrow k_{\text{In}} \cdot \downarrow [\text{ROO}^\bullet][\text{InH}]$$

Summarizing, it may be stated that the sensitivity of the reaction related to variations in the rate of an individual step and in the rate constant for the same step, by nature represent different concepts, which may differ substantially.

2. Sensitivity analysis provides the data at narrow-changing intervals in the values of the reaction rate constant of a complex reaction and is specified as the "local" analysis method. At the same time *a priori* determining the values of these intervals is not possible. However, if the densities of distribution by the values of steps of the rate constants $P_j(k_j)$ are assigned, then the task of sensitivity analysis becomes the calculation of density distribution $P_i(c_i)$. Such an approach is known as the method of

“global” sensitivity analysis. To get detailed information about the numerical methods of the “global” sensitivity analysis one can refer to [7,53-58].

In conclusion it should be noted that by focusing attention on the mentioned problems, we had the objective of gaining not only a more fundamental understanding of the capabilities of the sensitivity analysis method, but also of attracting attention to approaches that may complete undoubtedly this very promising method.

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Chapter 3

VALUE ANALYSIS OF KINETIC MODELS FOR CHEMICAL REACTION SYSTEMS

This chapter describes the theoretical basis of the *value* method of analysis for the mechanisms of complex (multistep) chemical reactions. *Value* approach is successfully implemented in the frame of numerical studies. On the base of specific examples, discussed are the opportunities and the distinguishing feature of the *value* method for solving the following principal tasks: a) modeling a complex reaction, b) reducing the number of non-essential individual steps and chemical species in kinetic models, and c) predicting reaction behavior. In so doing, it is possible, according to selected particular criterion, to identify the base (minimum) reaction mechanism by reducing the non-essential individual steps and reaction species.

The basis of the *value* approach is a Hamiltonian systematization of the mathematical model of a complex reaction with the extraction of the characteristics (functional) of a target reaction and with the kinetic comprehension of conjugate variables. Regardless of a reaction's complexity, pivotal in this approach is a universal numerical determination of kinetic trajectories of *value* units (the kinetic significance) of individual steps and chemical species of a complex reaction, according to the selected target reaction characteristic.

The *value* quantities for individual steps and reaction species characterize the response of output parameters at a certain time t , on the variation of rates of individual steps and rate-of-production of species at the initial time. The *values* of individual steps are functionally linked to the *values* of species involved in this step by the chemical equations of that step. In contrast to the sensitivity analysis, which evaluates the response of the reaction system on the rate constants of individual steps, in the *value* method varied are just the rates of individual steps and the rate-of-production of species of a complex reaction. The systemic link between the "elements" (the individual steps and species) of a reaction mechanism is realized not only by the quantities of the rate constants of steps, but also by the initial and intermediate concentrations of reaction species. These two magnitudes are present in the kinetic equation for the rates of individual steps and the rate-of-production of species in a complex reaction. Therefore, the *value* quantities more fully characterize the system-dependent quantities, such as the kinetic significance of species and reaction individual steps. By a simple example of a two-step sequential first-order reaction it is demonstrated in a greater degree the aiming of sensitivity parameters on identifying the rate-limiting steps, as compared with the *value* quantities.

In this and next Chapters fundamentals on the *value* analysis of chemical reaction systems are stated. Identification of kinetic significance of the reaction steps and chemical species is of great importance in such an approach. In its turn this task is related with solving the following key issues cited in Chapter 2 and presented below schematically

In many respects the diagram in Figure 3.1 determines the subsequent structure of contents. Before moving to interpret the main issues, let us mention briefly the principal statements serving as the basis for the development of a new analysis method for the kinetic models of chemical reaction systems.

Urgency of the problem requires developing:

- new mathematical methods of analysis for kinetic models of multistep reactions, which would be harmonized with the computational tools;
- new numerical criteria, easily interpretable from the physicochemical point of view to evaluate the kinetic significance of chemical species and the individual steps of kinetic models for complex chemical reaction systems;
- new methods of analysis for kinetic models that harmonize closely with problems of their *optimal control*.

Within the framework of the *value* approach, the kinetic significance of individual steps is determined by the *value* magnitudes. Specific feature of these *values* is that they are aimed at identifying an influence of the rate variation of steps or the the rate-of-production of reaction species on the magnitude of the output reaction parameter.

The system interdependence of individual steps is being identified to a great extent when varying the rates of individual steps. The *value* identification of step significance takes into account the interconnection of the given step with other ones, both by means of the value of the rate constant and immediately through the concentrations of species involved in the step. It enables to avoid some complications arising at determining the role of the steps by means of the rate constants' variation for steps, as it is implemented within the sensitivity analysis method (see Chapters 2 and 3). We also proceed from consideration that the proposed method must provide an opportunity to study such important features of the kinetic model of a complex reaction as its critical state, i.e. when the nature and reaction rate are qualitatively changed due to the small variations of initial conditions.

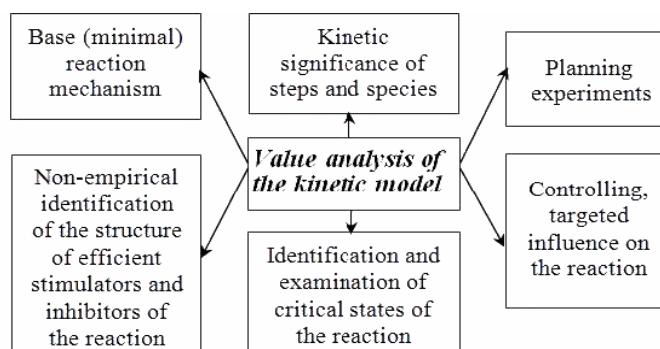


Figure 3.1. Diagram describing solvable research tasks and applicability areas of the *value* method to analyze reaction kinetic models.

3.1. THEORETICAL PREREQUISITES

3.1.1. Value Quantities

Quantitative changes in the concentration of chemical species with time in a spatially homogeneous reaction system under isothermal conditions may be described by a system of ordinary differential equations

$$\frac{dc_i}{dt} = f_i(\mathbf{c}, \mathbf{k}) \quad i = 1, 2, \dots, m, \quad (3.1)$$

where $\mathbf{c}(t)$ is the m -dimensional vector of species concentrations with $\mathbf{c}(t_0) = \mathbf{c}^0$, \mathbf{k} is the n -dimensional vector of the rate constants. The functions $f_i(\mathbf{c}, \mathbf{k})$ is the rate-of-production of species i contain the linear combination of the rates of individual steps, r_j , represented by

$$r_j = k_j \prod_{l=1}^m c_l^{a_{jl}}, \text{ where } a_{jl} \geq 0 \text{ and } \sum_{l=1}^m a_{jl} \leq 3. \quad (3.2)$$

$$f_i(\mathbf{c}, \mathbf{k}) = \sum_j v_{ij} r_j,$$

where v_{ij} is the stoichiometric coefficient of the i -th species in the j -th reaction.

To describe the phenomenon of selective initiation and inhibition of chain chemical reactions in [1] and later in [2-13], the concept of *step value* in a complex chemical reaction was introduced in a more general viewpoint. The *value* of an individual step is defined as the relation of the response of a chosen characteristic dynamic parameter of a reaction system, at some time t , to small perturbation of the j -th step rate at zero time, t_0 . Here, the step rate is varied by changing the initial conditions (the concentrations of initial substances, the reaction rate constants, etc.). In such cases the following expression is true for the *value* of the G_j step

$$G_j(t) = \frac{\partial F[r_1(t), \dots, r_n(t)]}{\partial r_j} \Big|_{r_j = r_j(t_0)}, \quad (3.3)$$

where $r_j(t)$ is the rate of the j -th step, $F(t)$ is the dynamic output parameter (the step rate, the changing rate of the reaction species concentration, the instant reaction selectivity and so on). The integral behavior of this specifies the selected target parameter, for example, the concentration of species, the yield of products, the deceleration period, the criticality of the reaction system, etc.

Similarly the *value* of the reaction system species is defined as the response of a selected target parameter at time t , to a small perturbation of the rate-of-production of species i at time t_0

$$\psi_i(t) = \frac{\partial F[f_1(t), \dots, f_n(t)]}{\partial f_i} \Big|_{f_i = f_i(t_0)}, \quad (3.4)$$

where $f_i(t) = dc_i/dt$ is the rate-of -production of the i -th reaction species.

Value quantities of the species and individual steps are strictly interconnected through chemical equations of individual steps in the following form:

$$\sum_l a_{jl} L_l = \sum_p a_{jp} P_p$$

where a_{jp}, a_{jl} are the stoichiometric coefficients for the j -th step, and p and l are the indices pertinent to the products and the initial compounds of the j -th step, respectively, L and P note the initial compounds and reaction products.

It follows from (3.3) and (3.4) that *the value of the j -th step is equal to the difference of values of the species generated and participating in this step, taking into account the stoichiometric coefficients*

$$G_j(t) = \sum_{i=1}^m \psi_i(t) \frac{\partial f_i}{\partial r_j} = \sum_p a_{jp} \psi_{jp}(t) - \sum_l a_{jl} \psi_{jl}(t). \quad (3.5)$$

It follows from (3.5) that the j -th step favorably effects on the increase of the output parameter of the reaction, if the products formed in this step have a higher *value*, as compared with the initial species of the step. We define the *value contribution* of a step at the selected output dynamic parameter of a reaction by:

$$h_j(t) = G_j(t) \cdot r_j(t), \quad j = 1, 2, \dots, n. \quad (3.6)$$

When defining the contribution of an individual step, we proceed from the assumption that the rate of such a step is not yet decisive from the viewpoint of its kinetic significance. Here the *value* parameter of a step also plays a vital role. Expressions (3.6) for estimating the contribution of an individual step are discussed below, where the calculational methods for the *value* magnitudes are described.

Similarly the *value* contribution of the i -th reaction species may be defined by

$$b_i(t) = \psi_i(t) \cdot f_i(t), \quad i = 1, 2, \dots, m. \quad (3.7)$$

In summary it may be said that for the assessment of kinetic significance for an individual step by the *value* method it is necessary to take into account at first the *value* quantities of individual steps G_j, h_j , and then *value* quantities of the species participating in the step according to the equation. The steps with small G_j, h_j and small *values* for the species ψ_j of this step are considered as unimportant. This allows to avoid random incorrect

assessment for an unimportant individual step conditioned by small G_{jk} which is a difference of two large quantities of ψ_j .

3.1.2. Calculation of *Value* Parameters

Based on the definition (3.4) let us find the equations enabling to calculate the time profiles of *values* in a suitable form. Here as a basis is accepted the method of *value* calculation through the conjugated functions [14] by using the *Hamiltonian description of dynamic systems* with marking out target characteristics.

Let us represent the selected attribute or, in other words, the *target functional* of a chemical reaction in an integral form

$$I(t) = \int_{t_0}^t F(t) dt. \quad (3.8)$$

Naturally, there is an opportunity of wide choice for the target functional of a chemical process and obviously the step contribution is dependant on the property of a complex chemical step selected as the first priority. If the aim is to identify the role of steps in the kinetics of the i -the species concentration's change, then the target functional may be represented as:

$$I(t) = \int_{t_0}^t f_i(t) dt. \quad (3.9)$$

But if the contribution of individual steps in the kinetics of the concentration variation of several reaction species is to be identified, then the target functional takes on the form

$$I(t) = \sum_i \int_{t_0}^t f_i(t) dt. \quad (3.10)$$

In the case when the selectivity of forming a certain (i -th) reaction product is chosen as the target functional (see Section 4.1), then

$$I(t) = \int_{t_0}^t (f_i + f_E) dt, \quad (3.11)$$

where $f_E(t)$ is the rate of the concentrations change of the initial reaction species. If the number of species for a reaction system equals m , then (3.4) transforms to

$$\psi_i(t) = \frac{\partial F}{\partial f_i}, \quad i = 1, 2, \dots, m, \quad (3.12)$$

or in an integral form

$$F = \sum_{i=1}^m \psi_i f_i + \text{const.}, \quad (3.13)$$

Let us denote the Hamiltonian function by

$$H = -F + \sum_{i=1}^m \psi_i f_i. \quad (3.14)$$

Comparing (3.13) and (3.14) gives $H = \text{const}$, consequently

$$\frac{dH}{dt} = \sum_i \left(\frac{\partial H}{\partial c_i} \frac{\partial c_i}{\partial t} + \frac{\partial H}{\partial \psi_i} \frac{\partial \psi_i}{\partial t} \right) = 0. \quad (3.15)$$

Whereas, according to (3.13), the system of kinetic equations (3.1) may be written as

$$\frac{dc_i}{dt} = \frac{\partial H}{\partial \psi_i} = f(\mathbf{c}, \mathbf{k}), \quad i = 1, 2, \dots, m \quad (\text{kinetic equations}) \quad (3.16)$$

and from (3.15) we obtain

$$\frac{dH}{dt} = \sum_i \left(\frac{\partial H}{\partial c_i} + \frac{d\psi_i}{dt} \right) \frac{dc_i}{dt} = 0. \quad (3.17)$$

Condition (3.17) shall be satisfied for arbitrary concentrations c_i . This leads to

$$\frac{d\psi_i}{dt} = -\frac{\partial H}{\partial c_i} \quad (\text{conjugate equations})., \quad (3.18)$$

It follows from (3.14), (3.16) and (3.18) that H represents well-known *Hamiltonian function* in the calculus of variations.

Values of the species $\psi_i(t)$ are determined by solving the system of equations (3.18) jointly with the kinetic equations (3.16). Then the *values* and step contributions are calculated from (3.5), (3.6) and (3.7), respectively. The initial magnitudes, $\psi_i(t_0)$, required for the calculation of *values* are determined, taking into account the chosen parameter F in the target

functional (3.8). For the sake of convenience in calculating $\psi_i(t_0)$ the output parameter F is represented as the linear combination of the rate-of-production of reaction species f_i according to the selected target.

Concerning the validity of expressions (3.6) and (3.7), specifying the *value* contributions of individual steps and species, respectively, let us transform (3.14) into

$$F = -H + \sum_j^n G_j r_j = -H + \sum_j^n h_j = -H + \sum_j^m \psi_i f_i = -H + \sum_j^m b_j . \quad (3.19)$$

It follows from (3.19) that equation (3.6) and (3.7) are accurate within a constant magnitude for definition of the relative contribution of an individual step and a chemical species in the chosen output parameter F of the reaction system. They also enable to predict accurately the behavior of the parameter F when the step rates and concentrations of species are varied. In fact, equation (3.19) enables to see clearly their physical significance.

Thus, the procedure for calculating the *value* magnitudes comes to the following milestones:

- a) writing down the target functional for a complex reaction, equation (3.8) and the proper Hamiltonian function of the system, equation (3.14);
- b) constructing the systems of kinetic equations (3.1), and differential equations for the $\psi_i(t)$ functions (the *values* of species) conjugated to species concentrations according to equation (3.18);
- c) determining the magnitudes of conjugated functions $\psi_i(t_0)$ corresponding to species at zero time, based on the target functional (3.8);
- d) calculation of the dynamics for ψ_i quantities by the combined solution of the system of kinetic equations (3.1) with the differential equations of conjugated functions (3.18);
- e) calculation of the time dependences for the *values* and *value* contributions of steps and species by equations (3.5)–(3.7), respectively.

The kinetic significance of individual steps and species are determined by the *value* method in the narrow interval of changing the rates of steps and accumulation of species. In other words, in such an interpretation, the *value* approach is a local analysis method. Likewise in the method on local sensitivity analysis, *a priori* determining the width of this interval is impossible. However, as it will be shown in Chapter 4, the *value* method allows to use it as a tool for finding the extremal (optimal) state of a reaction. At the same time this enables to calculate the *value* contributions of steps and reaction species, corresponding to the extremum of the target function. At that, the extremal value of the target function of the reaction may be found within a wide interval of varying the reaction parameters.

Summarizing, it should be emphasized that the offered *value* method to identify the significance of steps and species in the kinetic models of chemical reactions should be considered as complementary to the existing and proven approaches. Nevertheless, we hope that in a number of cases the *value* approach may produce certain advantages at analyzing

kinetic models, due to the simplicity of calculations and the obviousness of the data obtained. We shall try to give additional arguments concerning this issue in subsequent sections.

3.2. Determination of the Base Mechanism for a Complex Chemical Reaction. Application of the *Value* Method for Reduction of Reaction Mechanisms

Designing the appropriate kinetic scheme, which consists of a set of elementary transformations, is a main step to identify reaction mechanisms. In fact, this is the stage of setting up a hypothesis. Here two different approaches are applicable. The first may be called “*inductive*” and the second “*deductive*”.

When applying the *inductive approach*, the reaction mechanism is suggested (often in the hope of its uniqueness) based on the available experimental kinetic data for the reaction under study, the kinetic processing of these data and the information on the reactivity of possible reaction species. Obviously, in this approach some doubts always remain (particularly for quite complicated reaction mechanisms) concerning the adequacy and uniqueness of the reaction mechanism in the description of experimental data.

The *deductive method* is also based on the experimental kinetic data and the available information on the reactivity of reaction species, but proceeds from the maximum possible large scheme of the reaction. Further the procedure on *simplification (reduction)* of the reaction scheme follows, containing an excessive number of inessential reaction steps. Such a procedure implies the application of special mathematical methods, the performance of new experiments, and the comparison of descriptive capability for various options of the simplified reaction models. Only after that a conclusion is made about the correctness of the reaction kinetic model (see Figure 3.2).

It seems evident that the deductive method is more promising. The same conclusion can be made analyzing the literature on applying the computational approaches in the chemical kinetics [15-18] and the philosophic investigations [19,20] as well.

Nevertheless, the choice of either strategy in many respects is dependant on the quantity and quality of the available information, on the reactivity of species and the rate constants of reactions. Due to the availability of reliable quantitative data for the reactions, with participation of possible species of a reaction system, recently it became possible to apply successfully a deductive approach for modeling the reactions on combustion [21-27], cracking [28,29], atmospheric processes [30-36] and others.

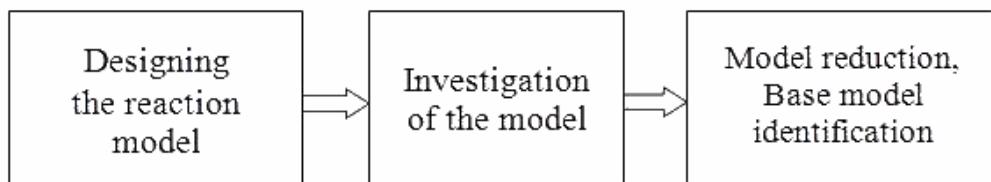


Figure 3.2. Formalized diagram of the “*deductive*” process for identification of the base kinetic model of chemical reactions.

It is also important that application of a “deductive” method enables to meet with a higher degree of confidence the following requirement: description of a large experimental data array at a specified high accuracy, when modeling a complicated chemical reaction, as well as the reliable prediction of objective laws of the reaction occurring under new conditions.

Often, when discussing the problem on setting up a primary hypothetical kinetic model of the reaction, it is commonly accepted to proceed from intuitive considerations. However, there exist the possibilities of setting up the hypothesis in a systematic way. A lot of publications are devoted to formalize the selection procedure for the modelling of complex chemical reactions on the basis of the combinatorial approach [17,18]. The described methods are based mainly on the construction of reaction schemes with different combinations of atomic and electronic rearrangements in the elementary steps. Then a screening of steps is carried out against definite criteria, namely: restricting the molecularity of steps, the number of atoms simultaneously changing the valency, the number of atoms in a molecule with unpaired electrons, the reaction endothermy and so on.

In addition, such a “deductive” procedure despite its evident usefulness is not able to bring to *a base (minimum) reaction mechanism*, to describe the experimental data with acceptable accuracy. The following is one of the principal reasons: a system factor is missed when the individual steps are rejected by means of such methods. Namely, the mutual influence of elementary transformations and the kinetic participation of steps in a complex chemical transformation are not taken into consideration. So, a situation is possible when the “improbable”, by the chosen criterion step, will have a considerable contribution in the progress of a complex chemical transformation. Therefore, the above-mentioned combinatorial approach has to be considered as the preliminary stage.

Prior to applying the methods to simplify the kinetic models of complex reactions, taking into account kinetic participation of the involved steps, we emphasize once again the importance of such a procedure. Finding the “base” kinetic model of a reaction is the identification of the fundamental essence of a chemical transformation. In fact, finding the “base” mechanism of the reaction is to reveal the nature of chemical transformation. The “base” reaction mechanism is some kind of “core”, which enables the in-depth understanding of the observed phenomena and highlights the fundamental ones.

Let us consider one more important aspect. Simplification of the reaction mechanism by elimination of unimportant constituents is one of the methods for the reduction of its mathematical dimensionality [35-40]. In other words, it leads to the reduction of the number of differential (kinetic) equations to be integrated, underlying the reaction mathematical model. Thus, it facilitates computational procedures, as well as it analyses the kinetic model, in terms of both its use of predicting the reaction behavior under new conditions and for its control. Not less important is also that at the available accuracy for the rate constants of individual steps, the descriptive capacity of kinetic models may decrease as its complexity increases (this question will be discussed more thoroughly in Section 3.3).

Later in Chapter 4 we will consider the task of how to control a chemical reaction by the use of its kinetic model. Such characteristics as concentrations of reagents, catalysts, temperature, pressure, etc. may be considered as the controlling parameters that influence a chemical reaction. It is clear that, in such cases *the base kinetic model of a reaction needs to be defined in the range of parameters listed, for which the controlling effect is realized. That is, the base kinetic model must be adequately controllable.*

Let us refer to another, in our viewpoint, important aspect in determining the base mechanism of a reaction. Attention should be focused on the fact that *the base mechanism of a reaction is also target-oriented*. Namely, the procedure for the simplification of a complicated reaction mechanism depends on how one selects the priorities of experimental effects of chemical reactions (the kinetic trajectories of concentrations of reaction species, the yield of target products, the criticality of reaction system, etc.). Therefore, those methods on kinetic model simplification that give also proper weigh to the target factor, for the description of complex chemical reaction behaviour, are thought to be promising.

Different methods on composing base reaction mechanisms to identify the kinetically insignificant steps are cited in the literature. Studies in this field are developed intensively. Noteworthy, in our opinion, are the approaches discussed below.

Analysis of the matrix of steps' stoichiometric coefficients according to the pathway theory. This method is supported by the corollaries of Horitui's theory for complex steady-state reactions discussed earlier in Chapter 2. As stated, in some cases the main fundamentals of this theory may be extended successfully to unsteady chemical processes. The main point of the matrix method, which simplifies kinetic models, consists in the selection (often using a PC) of the necessary set of pathways. The reduced kinetic model of a complex reaction is obtained by joining reaction paths with the chosen individual steps. Naturally, this process is strictly formalized [41,42]. It is remarkable that several mechanisms having the same pathway may be selected free of excessive ones. In such cases the selection is performed by using different criteria, for example, by considering their physicochemical significance. It should be emphasized also that this method does not require specifying the values of rate constants of steps. Nevertheless, it is unable to ensure the full reduction of "excessive" mechanisms, subject to ranking the role of steps.

Rate-of-production analysis. In the framework of this numerical method, to reject the steps throughout the whole process, usually a criterion is used, which characterizes the specific rate of a step in the overall rate-of-production of the reaction species, participating in a given step [43-48]

$$\left| r_{ij} \right| / \sum_{ij} \left| r_{ij} \right| < \varepsilon_{ij}, \quad i = 1, 2, \dots, m, \quad j = 1, 2, \dots, n, \quad (3.20)$$

where r_{ij} is the rate-of-production of the i -th species in the j -th step, and ε_{ij} is an arbitrary infinitesimal parameter.

Those steps are considered as candidates for elimination from the original reaction model, for which condition (3.20) is met over the whole process. The final positive answer on the possibility of eliminating a step from the reaction scheme is obtained, if the response parameter (selected in advance) of the chemical reaction is small, after excluding this step.

Meanwhile, when using the method under discussion, the following issues remain unexplained:

- the criterion for specifying the absolute value of the infinitesimal parameter ε_{ij} is not clarified;

- b) the parameter ε_{ij} is “insensitive” to the target selection, i.e. in no way concerns the issue, exactly what dynamic features of the chemical reaction a researcher is going to describe;
- c) the infinitesimal parameter in the portion of the step rate may itself be inappropriate, in evaluating the role of steps under critical conditions, when the parameters of a reaction change drastically, for small changes in some parameters and step rates.

Nevertheless, the step rate analysis method is applied successfully in combination with the sensitivity analysis method (see for example [33,46-49]) to be discussed below.

Analysis by applying the thermodynamic criterion. One has to face similar challenges when using the method to reduce an “excessive” kinetic model of a complex chemical reaction, based on the ideas of the step contribution in the reaction’s Gibbs free energy [50,51].

In the framework of such an approach *Lyapunov’s function* is used as a criterion, for the “selection” of steps by their significances:

$$\begin{aligned} q_s &= \dot{q}_s / \dot{q} \leq \varepsilon, \\ \dot{q}_s &= -r_s \ln(r_s^+ / r_s^-), \quad s = 1, 2, \dots, n, \\ \dot{q} &= -\sum_{s=1}^n r_s \ln(r_s^+ / r_s^-), \end{aligned} \quad (3.21)$$

where r_s, r_{-s} are the rates for the forward (s) and back ($-s$) steps, respectively; $q = G/V$ is the Gibbs thermodynamic potential per unit volume; and q_s specifies the thermodynamic portion of the s -th step in the variation of the reaction’s Gibbs free energy.

Similar approaches are also developed, defining the significance of individual steps by their contribution in the entropy change as a result of the total chemical reaction [51].

Sensitivity analysis method. To reduce the redundant steps in the kinetic model of chemical reactions, preference is mostly given to the method of sensitivity analysis, already described in Chapter 2. It was successfully applied in different areas of chemistry when studying the kinetic models of combustion reactions [21-28], cracking [28,29] atmospheric processes [30-33], self-oscillation reaction of Belousov-Zhabotinsky [52,53], and biological systems [54]. In addition to the given references one can find solutions of similar problems in [55-59].

This method is based on identifying a reaction’s insensitive to small changes in the rate constant values over the whole process. Further, the “insensitive” steps in the reaction scheme are determined by the elimination method. Practical invariability in the description of kinetic regularities of complex reactions (where the accuracy level is specified in advance), and the sensitivity range of the remaining reactions in the kinetic scheme usually validate the selection made.

The simplification procedure is facilitated by the simultaneous elimination of insignificant species, i , according to the criterion [29]

$$B_i = \sum_{k=1}^m \left(\frac{\partial \ln f_k}{\partial \ln c_i} \right)^2 < \varepsilon , \quad (3.22)$$

where ε is a small parameter chosen in advance.

If condition (3.22) is found to be satisfied over the whole process, then the i -th species may be excluded from the reaction scheme. Naturally, such a procedure helps to identify the redundant steps in the reaction kinetic scheme. One more important factor is related to the criterion (3.22), demonstrating the concentration interdependence between the reaction species, and consequently, between the different steps of a complex reaction. Such an interdependence is not immediately present in the parameters, which determine the step sensitivity. For this reason the simultaneous use of the step sensitivity criteria and the reaction species makes the process of reducing the reaction mechanisms more effective.

A more systematic approach for reducing the reaction kinetic model using the sensitivity analysis method, known as the method of *principal components analysis*, was developed by T. Turanyi and co-workers [56,57]. This method is applicable after calculation of the local sensitivity array and the compiling of the appropriate matrix from the normalized sensitivities

$$S = \left\{ \frac{k_j \partial y_i}{y_i \partial k_j} \right\} .$$

Further the data array entered into the matrix S is processed.

The main point of this approach is to apply the method of eigenvalues and eigenvectors analysis to obtain the kinetic pattern through the sensitivity parameters. Information extracted in such a manner for different reaction times enables to identify effectively the unimportant steps in the reaction kinetic model.

Let us again refer to the problem of “zero” sensitivity for an important reaction. To overcome this problem often it is necessary to take recourse to additional methods, among which is the above-mentioned analysis of reaction rates [46-49].

Computer-aided design method of the base reaction kinetic model. The computer-aided design method undoubtedly is one of the promising approaches to identify the base kinetic model of complex reactions. It was implemented by L.J. Broadbelt, S.M. Stark and M.T. Klein [60] by means of the “NetGen” software. A specific feature of the method is that it does not imply a reduction in the initially excessive models of chemical reactions. The latter realizes computer-aided design through the *build-up* of chemical species and reaction steps in the kinetic model. Here the design of the kinetic model itself is implemented by the trial method of kinetic importance of species and accordingly, the steps with their participation. It is easy to see that this approach is similar to the majority of the above described ones, in terms of the same specific feature, which is based on the identification of kinetic significances of species and steps of a reaction mechanism.

The method of designing the kinetic models of reactions suggested by W. Green and co-workers [61] through the *estimation* of the rate-of-production of chemical species i seems to

be of special attraction. Here the used criterion for the kinetic significances of the species is similar to that applied in the above-described method of the step rates analysis.

In general, the main point of the method is as follows:

1. The process of designing the reaction base model starts with the initial kinetic model involving a small set of species.
2. Then the important “reactive” species are identified according to a criterion taking into consideration the rate characteristics $r_i > r_{\min}$. Here r_i and r_{\min} represent the maximum rate of the i -th species and the minimum significant accumulation rate of the reaction species, respectively. In turn, r_{\min} is defined by:

$$r_{\min} = (\text{specified accuracy level of model performance}) \times r_{\text{char}}$$

$$r_{\text{char}} = K[A]_0 / \tau,$$

where r_{char} is the reaction characteristic (average) rate, K is the conversion of chemical reaction at time τ , and $[A]_0$ is the initial concentration for the reagent A.

3. In the case of high kinetic significance of some species, this is accepted as a “*reactive member*” of the base model. Simultaneously the computer examines all available reactions in memory that involve the given species. Consequently, this results in the generation of additional reaction species, not yet “reactive”, but a part of which may appear significant and fall into the category of “reactive” ones.
4. The procedure described in point 3 is repeated as long as among the newly generated (“non-reactive”) reaction species remain only the significant ones. As a result the reaction base kinetic model is designed involving only the significant chemical species.

The fact that while designing the base reaction mechanism by the above described method a large number of species is being looked over as compared to the final version of the kinetic model is thought to be of special importance. Naturally this provides a very large range for the deductive process. It is very important that the number of simultaneously integrated ordinary differential equations coincides just with the quantity of significant, but not the “looked over” reaction species. This is crucial for the computer-aided calculations.

As an illustration let us refer to the reaction of ethane pyrolysis [61]. The reaction base kinetic model at a specified accuracy level of 0.0001 consists of 180 species, while in its design stage 27076 species and 99644 reaction steps are considered.

In closing let us note an essential aspect, which is fairly pointed out by the authors of reference [61]. When looking over a large number of reaction steps the accuracy problem of the rate constant values for these steps becomes more acute (see also Section 3.3).

Value method for analysis of kinetic models. The *value* method is believed to be very promising when it is used to clarify the base kinetic model of a reaction. In determining the base mechanism by the *value* analysis the following specific features may be highlighted:

- As mentioned above, the *value* contributions of species b_i , and steps h_j , on the basis of which the unimportant steps are identified, in our opinion, are more meaningful and comprehensive for the description of kinetic significance of these parameters, from the physicochemical, kinetic standpoint. We remind that the response of a reaction system to variation in the rates of individual steps or the accumulation of reaction species reveals the system relationship between the species and steps simultaneously, through the species concentrations and the rate constants of steps, such that their kinetic significance is determined more completely.
- The available arsenal provides ways to address the task of establishing the reaction minimal mechanism. By selecting the appropriate target functionals (see Section 3.1) one can succeed to determine the base mechanisms “responsible” for the more specific features in the behavior of a multistep reaction.
- The *value* method allows also to identify the base mechanism under the critical state of the reaction system. The “role of steps” could change drastically under such conditions (see Chapter 5).

Summarizing the above we note that owing to distinctive features of the *value* method for analyzing reaction systems, the possibility of its wide use in designing the base kinetic model of a chemical reaction seems quite optimistic. Moreover, in combination with other methods, it expands the capabilities of researchers to develop efficient strategies to reduce the reaction mechanisms.

3.3. ON THE PROBLEM OF RELIABILITY HIERARCHY OF REACTION RATE CONSTANTS MAGNITUDES IN THE KINETIC MODEL

Reaction rate constants represent the quantitative base for the kinetic model of a chemical transformation. However, while some are quite accurate, the range of uncertainty of others is very broad. Overcoming this problem is a question of principle when studying the mechanism of a multistep chemical reaction.

Intuitively one can conclude that the degree of reliability for rate constant values determines the limits of complexity of reaction mechanisms, at the level of their design and analysis. This is entirely true also when selecting the strategy for the investigation of reaction mechanisms. In Section 3.2 such approaches are conditionally subdivided into “inductive” and “deductive” methods.

At present the importance of having a correct knowledge of the step rate constant values is indisputable. Therefore, no wonder that in the field of chemical kinetics, over the last decades, efforts were focused on the quantitative investigation of elementary reactions. It may be easily predicted that the situation with the quantitative information about elementary reactions will be improved progressively.

Nevertheless, problems arising due to the existing uncertainty in the values of step rate constants may be overcome to a great extent, by the studies of the same complicated reaction. It is appropriate to cite the opinion of the well-known chemist L. Kassel: “For lack of facts supporting one or another hypothesis, designing the reaction mechanism becomes a game, rather pleasant than useful” [62].

It is believed that one can achieve good reliability in describing complex reactions, if one combines “computer” experiments with detailed laboratory experimental studies. Here, applying the methods of solving inverse problems of chemical kinetics, aimed at updating the rate constant values for individual steps are also relevant [15,63,64].

Suitable combination of “computer” and experimental efforts enables us to use the “ping-pong” principle more effectively. We are already familiar with such an approach. In this case, the computer analysis and the “key” experiment are mutually complementary; as a result, the realistic reaction mechanism becomes apparent.

We suppose that the *value* method of analyzing the reaction kinetic models may enhance considerably the efficiency of a similar procedure, as it improves the capabilities to retrieve information from the kinetic models of reactions. On the other hand, this method enables to rank the steps, and accordingly, the rate constants of the kinetic model, by their “sensitivity” in describing specific experimental results. This will permit to determine acceptability of applying the rate constants with a prescribed accuracy. One can look through the analysis of uncertainty of the kinetic model due to the uncertainty of rate constant of steps in references [58,65,66].

3.4. APPLICATION OF *VALUE* ANALYSIS AT STUDYING THE PROGNOSTIC CAPABILITY OF THE KINETIC MODEL OF REACTION SYSTEM

Prognostic capability is an important feature of the kinetic model. It is determined by the range of change of parameters, which describe the conditions of a reaction progress (concentrations of reagents, catalyst, promoter, conversion of the initial reagents, pressure, temperature, etc.) outside of which the prognostic capability of the model fails.

Definition of the applicable range of the kinetic model of a chemical reaction is of special importance for its control. Theoretical methods for the optimal control of chemical processes will be considered in the next chapter. It is expedient to perform the controlling impact on a reaction by using a proper kinetic model, within the limits of change of the controlling parameters $\mathbf{u}(t)$, where it maintains its prognostic capability.

When modeling a chemical reaction, most often a researcher faces the challenge of broadening the prognostic capability of a kinetic model. *Value* analysis of the kinetic model may serve as a useful tool to solve such tasks. The main point is that when expanding the prognostic capability of a model by means of kinetic significance of the steps and chemical species, one can highlight the species and individual steps, which influence significantly on the predictive accuracy of the model. It becomes clear that the *value analysis* “*structures chemically*” the prognostic capability of the kinetic model. This permits to solve the following problems being fundamental in strengthening the prognostic capacity of the model:

- *to determine dominant parameters*, influencing on prognostic capability of the kinetic model, on which the research efforts should be focused. We faced a similar situation in the preceding Section, when we discussed approaches to overcome the problems of hierarchical reliability of step rate constants in a reaction mechanism.

- to perform *value* “structuring” of the prognostic capability of the kinetic model, which facilitates greatly the actions directed to improve this model’s indicator by means of its reconstruction. For example, the initial kinetic model may be more reasonably supplemented with new steps.
- to compare *value* contributions of steps under the conditions of experimentally studying the chemical reaction, and the conditions where the reaction behavior is predictable. This helps to plan new experiments aimed at updating the kinetic model. The pursued target is to attain a better agreement between the “spectra” of kinetic significances of steps for a multistep reaction, both for the experimental and predicted conditions. We think this may serve as a *reliability criterion for the prognosis on the behavior of a reaction system*. In other words, predictable high important individual steps have to be the same under experimental conditions, by which adequacy of the model is checked. Just such prediction will be reliable. The problem under consideration is of particular urgency when it is necessary to predict the reaction behavior out of the possible areas of experimental study. For example, if the adequacy of a kinetic model is verified by experiments, which take only a little time, whereas prediction is carrying out over incommensurably prolonged chemical transformations. Such a *value* investigation for the prognostic reliability of the kinetic model is illustrated by the example of ethylbenzene oxidation, which is inhibited by butylated hydroxytoluene (see Chapter 7). *Value* procedure for increasing the prognostic reliability is schematically demonstrated in Figure 3.3.

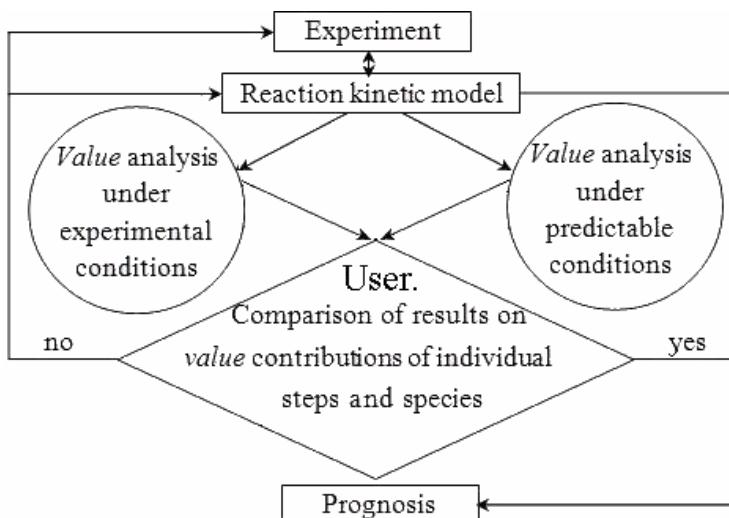


Figure 3.3. Formalized recording of procedures at *value* examination of prognostic reliability of the kinetic model for a multistep reaction.

Summarizing the above, it may be assumed that the *value* analysis together with examination of the parametric sensitivity may become a very effective tool to improve the prognostic reliability of kinetic models and to control the capabilities of such models.

3.5. EXAMPLES OF VALUE ANALYSIS OF KINETIC MODELS

In this Section three examples are discussed to illustrate the *value* identification of kinetic significance in the steps of complex reactions. For ease of understanding, the models of chemical reactions are considered in the order of their complication.

3.5.1. Consecutive Irreversible First-Order Reaction

A simple consecutive reaction (the case of two consecutive irreversible first-order reactions is selected as the first demonstration):



where A, B, C are chemical species of the reaction and k_1 , k_2 are the rate constants of individual steps.

This simple example is selected as it enables to demonstrate more clearly the output numerical data of the *value* analysis for a reaction mechanism.

For comparison the analysis of local parametric sensitivities widely used in analysis of complex reaction mechanisms was selected as a “benchmark” numerical method.

Value analysis consists in determining the kinetic significances of steps by specifying the influence of change in the initial rates of the individual steps on the kinetics of accumulation of the final product, C.

To calculate the dynamics of changes in *value* contributions of individual steps, the Hamiltonians for the appropriate target functionals are expressed in terms of the species C. The appropriate concentrations of the consecutive reaction species are selected as the functionals, I . According to (3.10) and (3.14) these target functional and the Hamiltonian are the following:

$$I_C = \Delta[C] = \int_0^t f_C dt, \quad H_C = -f_C + \psi_A f_A + \psi_B f_B + \psi_C f_C$$

In compliance with the selected target functional (I_C) the relevant initial conjugate functions ψ_i are defined, as required for the integration of the differential equations (2.12).

For I_C : $\psi_C(t_0) = 1$; $\psi_A(t_0) = \psi_B(t_0) = 0$

Time trajectories of *value* contributions for the individual steps (h_j) are determined by equations (3.16) and (3.18). Eventually in calculations the reduced values of the *value*

contributions become defined in the form: $\overline{h_j(t)} = h_j(t) / \sqrt{\sum_{j=1}^2 h_j^2(t)}$.

Analysis of the relative sensitivities for the steps (S_C) are carried out by calculating the ratio of the response of the concentration change ($\Delta[C]$) of the reaction species at time t to the

small change (1%) in the reaction rate constants (Δk_i). For reactions $A \xrightarrow{k_1} B$ and $B \xrightarrow{k_2} C$: $S_C = \frac{k_i \Delta [C]}{\Delta k_i [C]}$, $i = 1, 2$.

Table 3.1

Ratio of rate constants of the steps	k_1	k_2	$k_1 = k_2$	k_1	k_2
Rate constants of the steps	$k_1 = \tau^{-1}$		$k_1 = \tau^{-1}$	$k_1 = \tau^{-1}$	
		$k_2 = 100\tau^{-1}$	$k_2 = \tau^{-1}$		$k_2 = 0.01\tau^{-1}$

Numerical analysis of the kinetic significances of the individual steps in the simple consecutive reaction is carried out for the three ratios of the rate constants, in terms of the reduced values τ^{-1} ($\tau^{-1} = k_1$), in units of s^{-1} (see Table 3.1).

The following initial concentrations of the species are used to calculate: $[A]_0 = 1$ M; $[B]_0 = 0$ M; $[C]_0 = 0$ M.

Analysis of Accumulation Kinetics for the Reaction Product C

The relative sensitivity parameters and the *value* contributions of individual steps are presented in Figure 3.4 for the case when their role in the kinetics of the accumulation of the final product (C) is identified.

As follows from results shown in Figure 3.4, the method of sensitivity analysis in this case is an efficient tool to identify the rate-controlling step of the total process. So, for the case when $k_1 \ll k_2$ the relative sensitivity of the second step $B \rightarrow C$ tends to zero after a short period of time, whereas that for the step $A \rightarrow B$ with comparatively lower value of k_1 retains a high value throughout the reaction. Thus, the high value of relative sensitivity clearly highlights the step $A \rightarrow B$ as the rate-controlling one. A similar picture is observed for the case when $k_1 \gg k_2$. This significantly higher value of the relative sensitivity for the step $B \rightarrow C$ unambiguously identifies it as a step, limiting the chemical process of the formation of final product, C.

For the case when $k_1 = k_2$ the values of the relative sensitivities are commensurable, so it is difficult to suggest about the limiting role of a certain step.

Thus, the sensitivity analysis reveals unambiguously the rate-limiting steps of a complex chemical transformation. Meanwhile, a near-zero value of the relative sensitivity of an individual step, as obviously it should be considered from the discussed simple example of the consecutive reaction, does not allow to eliminate it from the reaction mechanism. As mentioned above, the reduction of the reaction mechanism is an actual problem as it allows revealing the kinetically inessential steps.

Let us now turn to the results of the *value* analysis. When considering the role of the steps in the kinetics of the final product accumulation, the time profiles of the reduced *value*

contributions give the same kinetic significance for the both steps of a consecutive reaction. This emphasizes the need to have the mandatory "presence" of both steps in the mechanism that describes a simple consecutive reaction.

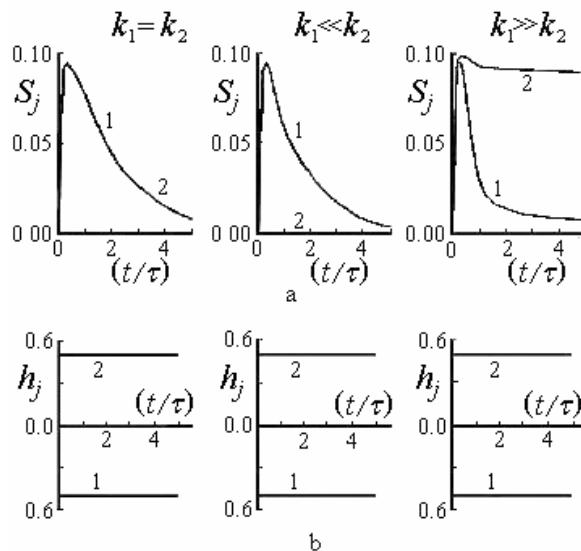


Figure 3.4. Calculated time trajectories of local sensitivities (a) and reduced *value* contributions (b) for the steps $A \xrightarrow{k_1} B$ (1) and $B \xrightarrow{k_2} C$ (2) of the consecutive reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ in identifying their role in the accumulation kinetics of the final product C.

A negative magnitude of the *value* contribution $\overline{h_{C,1}}$ is associated with different signs of the rate of concentration change at the initial time between the initial species A on the one hand, and the reaction products B and C, on the other. Undoubtedly, if for the *value* contributions not reduced but absolute magnitudes of *value* contributions for the steps 1 and 2 were used, the values $h_{C,1}$ and $h_{C,2}$ would decrease symmetrically with time, tending to zero (see equation (2.6)) owing to the nullification tendency in the rates of individual steps during the reaction.

Conclusion

In considering a simple consecutive reaction, the method of analysis of local sensitivities and *value* analysis yield similar results when evaluating the kinetic significance of individual steps.

At the same time the method of sensitivity analysis seems to be more correct in the identification of the rate-limiting steps of multistep reactions. However, this method may face the problem of "zero" sensitivity. That is, when throughout the process a zero value of the sensitivity, relative to the change in the rate constants of the step, not always enables uniquely to characterize it as "excessive" and to exclude from the kinetic model of the reaction aimed at its reduction. To solve such a problem there is a need to attract additional tools [57,58].

In contrast, the *value* analysis is more focused on the construction of a basic kinetic model by excluding the excessively low-value steps from the expanded primary reaction model.

3.5.2. Ozone Kinetics

As an example let us refer to Chapman's mechanism for the kinetics of atmospheric ozone transformations [67], presented in Table 3.2. A choice is conditioned by very carefully testing the sensitivity analysis method on this example [68, 69]. It seems interesting to compare the data from [68, 69] with the results of the *value* identification of step significances [7,10].

The initial concentrations are as follows: $[O]_0=10^6$, $[O_3]_0=10^{12}$, $[O_2]_0=3.7 \cdot 10^{16}$ particle \cdot cm^{-3} .

To identify the contributions of individual steps let us write the target functionals in the form [2-13]

$$I_1(t) = \Delta[O]_t = \int_{t_0}^t f_O dt, \quad I_2(t) = \Delta[O_3]_t = \int_{t_0}^t f_{O_3} dt. \quad (3.23)$$

Here f_{O_3}, f_O are the rates-of-production of ozone and oxygen. The corresponding Hamiltonians in accordance with (3.23) may be written as

$$\begin{aligned} H_1 &= -f_O + \psi_O f_O + \psi_{O_3} f_{O_3} + \psi_{O_2} f_{O_2}, \\ H_2 &= -f_{O_3} + \psi_O f_O + \psi_{O_3} f_{O_3} + \psi_{O_2} f_{O_2}. \end{aligned} \quad (3.24)$$

Then equations (3.1) and (3.18) take on the following forms:

$$\begin{aligned} \frac{d[O]}{dt} &= -k_1[O][O_2] - k_2[O][O_3] + 2k_3[O_2] + k_4[O_2], \\ \frac{d[O_3]}{dt} &= k_1[O][O_2] - k_2[O][O_3] - k_4[O_3], \\ \frac{d[O_2]}{dt} &= -k_1[O][O_2] + 2k_2[O][O_3] - k_3[O_2] + k_4[O_3] \end{aligned} \quad (3.25)$$

For target functional I_1

$$\begin{aligned} \frac{d\psi_O}{dt} &= \{k_1[O_2] + k_2[O_3]\}\psi_O - \{k_1[O_2] - k_2[O_3]\}\psi_{O_3} + \\ &\quad + \{k_1[O_2] - 2k_2[O_3]\}\psi_{O_2} - k_1[O_2] - k_2[O_3], \\ \frac{d\psi_{O_3}}{dt} &= \{k_2[O] - k_4\}\psi_O + \{k_2[O] + k_4\}\psi_{O_3} - \\ &\quad - \{2k_2[O] + k_4\}\psi_{O_2} - k_2[O] + k_4, \end{aligned} \quad (3.26)$$

$$\frac{d\psi_{O_2}}{dt} = \{k_1[O] - 2k_3\}\psi_O - k_1[O]\psi_{O_3} + \{k_1[O] + k_3\}\psi_{O_2} - k_1[O] + 2k_3,$$

Table 3.2. Kinetic model of ozone transformation

No	Steps	Rate constants*
1	$O + O_2 \rightarrow O_3$	$1.63 \cdot 10^{-16}$
2	$O + O_3 \rightarrow 2O_2$	$4.66 \cdot 10^{-16}$
3	$O_2 \rightarrow 2O$	$5.0 \cdot 10^{-11}$
4	$O_3 \rightarrow O + O_2$	$2.5 \cdot 10^{-4}$

* Rate constants are presented in the units: number of particles, cm, s. The reactions 1-4 involve an additional particle M.

For target functional I_2

$$\begin{aligned}
 \frac{d\psi_O}{dt} &= \{k_1[O_2] + k_2[O_3]\}\psi_O - \{k_1[O_2] - k_2[O_3]\}\psi_{O_3} + \{k_1[O_2] - \\
 &\quad - 2k_2[O_3]\}\psi_{O_2} + k_1[O_2] - k_2[O_3], \\
 \frac{d\psi_{O_3}}{dt} &= \{k_2[O] - k_4\}\psi_O + \{k_2[O] + k_4\}\psi_{O_3} - \\
 &\quad - \{2k_2[O] + k_4\}\psi_{O_2} - k_2[O] - k_4, \\
 \frac{d\psi_{O_2}}{dt} &= \{k_1[O] - 2k_3\}\psi_O - k_1[O]\psi_{O_3} + \{k_1[O] + k_3\}\psi_{O_2} + k_1[O].
 \end{aligned} \tag{3.27}$$

The system of conjugate differential equations (3.26) and (3.27) are attributed to the functionals I_1 and I_2 , respectively. For I_1 the initial values of ψ_O , ψ_{O_3} , ψ_{O_2} are equal to (1,0,0), respectively, and for I_2 they are (0,1,0). Kinetic trajectories for ψ_O , ψ_{O_3} , ψ_{O_2} were determined by resolving the system of differential equations (3.25), (3.26) for I_1 , and (3.25), (3.27) for I_2 . On the basis of obtained data for conjugate functions, time dependences for the reaction contributions were calculated by equations (3.5) and (3.6)

$$\begin{aligned}
 h_1 &= (\psi_{O_3} - \psi_O - \psi_{O_2})r_1, \quad h_2 = (2\psi_{O_2} - \psi_O - \psi_{O_3})r_2, \\
 h_3 &= (2\psi_O - \psi_{O_2})r_3, \quad h_4 = (\psi_O + \psi_{O_2} - \psi_{O_3})r_4.
 \end{aligned} \tag{3.28}$$

To calculate numerically the time profiles of the concentrations for the reaction species, as well as the *value* contributions of species and individual steps, our own-developed VALKIN software was applied. VALKIN employs the program ROW-4A [70] to solve the system of differential equations. This is described in detail in Chapter 9.

Kinetic curves on the change of ozone and oxygen atom concentrations are presented in Figure 3.5, while Figures 3.6 and Figures 3.7 illustrate the calculation data for the time profiles of contributions of individual steps in relative units for the I_1 and I_2 functionals.

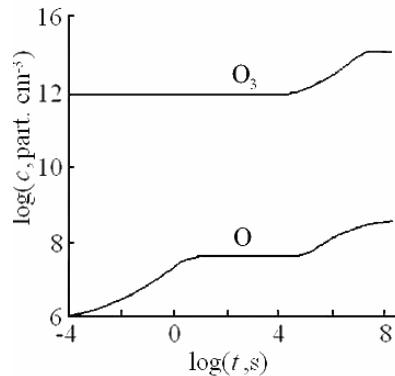


Figure 3.5. Dependences of $\log[\text{O}]$ and $\log[\text{O}_3]$ vs. $\log(t)$ for the kinetics of ozone transformation.

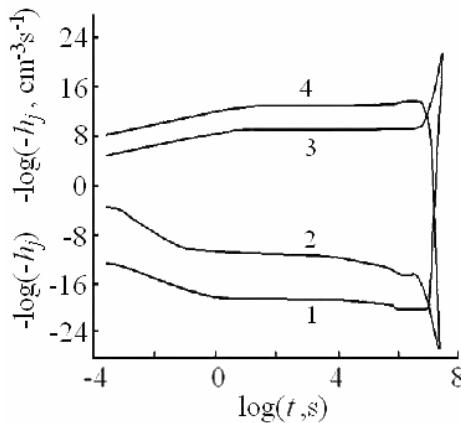


Figure 3.6. Kinetic trajectories of *value* contributions of individual steps for the target functional I_1 . Curves are numbered according to steps in Table 3.2.

The results of the *value* approach agree sufficiently with the data from J. Hwang [68,69], which are obtained with application of the sensitivity analysis for rate constants of steps. In [68, 69] the step sensitivity was determined by $S_j = k_j \partial c / c \partial k_j$, where k_j is the rate constant of the j -th reaction, $c = [\text{O}]$ or $[\text{O}_3]$.

As may be seen from Figures 3.6 and 3.7 within the time interval $3.6 \cdot 10^6$ to $6 \cdot 10^6$ s, an abrupt change in the individual step *value* contributions is observed. Incidentally, this time interval was not studied in [68,69]. Such behaviour of step *value* contributions was validated by direct calculations, showing drastic changes in the concentrations of species for this time interval, caused by small changes in the step rate constants. Some disagreement between the results by these two methods is due to the difference in evaluating the kinetic significances of individual steps. The differences may be still more when analyzing more complicated reaction mechanisms. As mentioned above, the reason is in different response of some resultant characteristic of a chemical reaction depending on what parameter, rate or rate constant of reaction step is varying. We think the role of an individual step is identified more completely when the response of a reaction system, namely on the variation in the rate of this individual step, is determined.

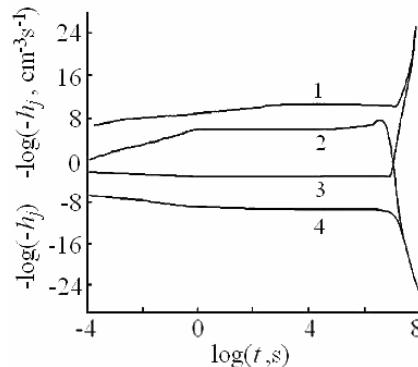


Figure 3.7. Kinetic trajectories of contributions of individual steps for the target functional I_2 . Curves are numbered according to steps in Table 3.2.

3.5.3. Reduction of Reaction Mechanism for Gas-Phase Oxidation of Formaldehyde in the Presence of Carbon Oxide (II)

Reaction mechanism for gas-phase oxidation of formaldehyde in the presence of carbon oxide (II), suggested by I.A. Vardanyan, G.A. Sachyan, A.B. Nalbandyan [71] and presented in Table 3.3, is rather complicated. However, it is chosen deliberately as a useful one for the clarification of the methods to reduce kinetic models, based on the sensitivity analysis method [28,56,69].

The chosen kinetic model seems to be convenient for revealing the capabilities of the *value* method and the comparative analysis of the data obtained by different methods.

Based on selected data array on the sensitivity of species concentrations for the rate constants of steps at the reaction time $5 \cdot 10^{-3}$ s, E.P. Dougherty, J.T. Hwang, H.G. Rabitz [69] determined both the dominant and unimportant steps of the reaction mechanism, as presented in Table 3.3. Further, using a more systematic method to analyze data on the sensitivity of concentrations [56] and rate-of-production of the reaction species [28], with respect to variations of the step rate constants (the method of principal components analysis) S. Vajda, P. Valko, T. Turanyi [56] ranked the role of steps for the reaction mechanism of gas-phase oxidation of formaldehyde in the presence of carbon oxide (II). They succeeded also in separating the minimal reaction mechanism involving 13 steps, which gives the same results, accurate to within 2% (for the reaction time of $5 \cdot 10^{-3}$ s), as the initial kinetic model consisting of 25 steps (see Table 3.5).

Now let us schematically represent the stages laid down in the *value* analysis of the kinetic model for formaldehyde oxidation in the presence of carbon oxide (II). First let us choose the target functional characterizing the change in the concentration of the initial substances: formaldehyde, carbon oxide (II) and oxygen

$$I(t) = -\Delta[\text{CH}_2\text{O}]_t - \Delta[\text{CO}]_t - \Delta[\text{O}_2]_t = -\int_0^t [f_{\text{CH}_2\text{O}} + f_{\text{CO}} + f_{\text{O}_2}] dt \quad (3.29)$$

Table 3.3. Reaction mechanism for gas-phase chain oxidation of formaldehyde in the presence of carbon oxide (II)

No	Reactions	Rate constants*
1	$\text{H}\dot{\text{C}}\text{O} + \text{O}_2 \rightarrow \text{HOO}^\bullet + \text{CO}$	$1 \cdot 10^{-13}$
2	$\text{HOO}^\bullet + \text{CH}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{H}\dot{\text{C}}\text{O}$	$5.7 \cdot 10^{-14}$
3	$\text{H}_2\text{O}_2 + \text{M} \rightarrow 2\text{HO}^\bullet + \text{M}$	$6.66 \cdot 10^{-18}$
4	$\text{HO} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HOO}^\bullet$	$1.6 \cdot 10^{-10}$
5	$\text{HO} + \text{CH}_2\text{O} \rightarrow \text{H}_2\text{O} + \text{HC}^\bullet\text{O}$	$5.1 \cdot 10^{-12}$
6	$\text{H}_2\text{O}_2 \xrightarrow{\text{wall}} \text{nonradical products}$	1.05
7	$\text{HOO}^\bullet \xrightarrow{\text{wall}} \text{nonradical products}$	$1.05 \cdot 10^2$
8	$\text{HOO}^\bullet + \text{HOO}^\bullet \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$3.0 \cdot 10^{-12}$
9	$\text{HO}^\bullet + \text{CO} \rightarrow \text{CO}_2 + \text{H}^\bullet$	$3.3 \cdot 10^{-13}$
10	$\text{HOO}^\bullet + \text{CO} \rightarrow \text{CO}_2 + \text{HO}^\bullet$	$1.2 \cdot 10^{-15}$
11	$\text{H}^\bullet + \text{CH}_2\text{O} \rightarrow \text{H}_2 + \text{H}\dot{\text{C}}\text{O}$	$2.7 \cdot 10^{-12}$
12	$\text{H}^\bullet + \text{O}_2 \rightarrow \text{HO}^\bullet + \text{O}^\bullet$	$5.51 \cdot 10^{-14}$
13	$\text{H}^\bullet + \text{O}_2 + \text{M} \rightarrow \text{HOO}^\bullet + \text{M}$	$1.0 \cdot 10^{-32}$
14	$\text{HOO}^\bullet + \text{M} \rightarrow \text{H}^\bullet + \text{O}_2 + \text{M}$	$4.7 \cdot 10^{-19}$
15	$\text{O}^\bullet + \text{H}_2 \rightarrow \text{HO}^\bullet + \text{H}^\bullet$	$3.02 \cdot 10^{-13}$
16	$\text{O}^\bullet + \text{CH}_2\text{O} \rightarrow \text{HO}^\bullet + \text{HCO}$	$1.0 \cdot 10^{-10}$
17	$\text{H}^\bullet + \text{H}_2\text{O}_2 \rightarrow \text{HOO}^\bullet + \text{H}_2$	$1.3 \cdot 10^{-12}$
18	$\text{H}^\bullet + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}^\bullet$	$5.9 \cdot 10^{-12}$
19	$\text{O}^\bullet + \text{H}_2\text{O}_2 \rightarrow \text{HO}^\bullet + \text{HOO}^\bullet$	$1.0 \cdot 10^{-13}$
20	$\text{H}\dot{\text{C}}\text{O} \rightarrow \text{H}^\bullet + \text{CO}$	$4.6 \cdot 10^{-12}$
21	$\text{HO}^\bullet + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}^\bullet$	$1.0 \cdot 10^{-11}$
22	$\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{H}\dot{\text{C}}\text{O} + \text{HOO}^\bullet$	$2.9 \cdot 10^{-20}$
23	$\text{H}^\bullet + \text{HOO}^\bullet \rightarrow 2\text{HO}^\bullet$	$5.0 \cdot 10^{-12}$
24	$\text{H}^\bullet + \text{HOO}^\bullet \rightarrow \text{H}_2\text{O} + \text{O}^\bullet$	$5.0 \cdot 10^{-11}$
25	$\text{H}^\bullet + \text{HOO}^\bullet \rightarrow \text{H}_2 + \text{O}_2$	$4.5 \cdot 10^{-11}$

* Rate constant values are presented in units: number of particles, cm, s, at $T=679$ ^0C . The initial concentrations: $[\text{CH}_2\text{O}]_0=6.77 \cdot 10^{16}$, $[\text{O}_2]_0=1.27 \cdot 10^{18}$, $[\text{CO}]_0=2.83 \cdot 10^{18}$, $[\text{M}]=7.09 \cdot 10^{18}$ part.cm $^{-3}$.

Such a functional was selected with the intent to identify the role of steps of the reaction mechanism in the conversion of the initial reagents.

The system of differential equations (3.16) and (3.18) was solved for the following initial values of ψ_i . From the target functional (3.29) we have $\psi_{\text{CH}_2\text{O}}(0)=\psi_{\text{CO}}(0)=\psi_{\text{O}_2}(0)=-1$. For the remaining reaction species ψ_i equals to zero at zero time.

Table 3.4 displays the computed *value* contributions of steps $\{\bar{h}_j = h_j \left(\sum_{j=1}^n h_j^2\right)^{-1/2}\}$ for different reaction times, which were intentionally chosen to be the same as in [28, 56]: from 10^{-5} s (for 0.01% conversion of CH_2O) to $5 \cdot 10^{-3}$ s (for 1.23% conversion of CH_2O).

In Table 3.5 the rank of steps determined by the *value* method and the methods based on sensitivity analysis is presented. Additionally the base mechanism containing 13 steps, sorted out in [28, 56] is presented also.

Analyzing data from Tables 3.4 and 3.5 one can note that the first 14 steps involve the base mechanism of the reaction from the viewpoint of absolute *value* contributions. Relative contributions of excluded reactions are small ($\bar{h}_j \leq 10^{-4}$) at any reaction times considered. Note that step (14), not included in the base mechanism is ranked as only 13-th in the chosen range. Base mechanism of 14 steps including step (14) describes the kinetic trajectory of the hydrogen atom concentration with 4% deviation from the initial model, and deviation of 2.7% has been observed in [28, 56] for the base model of the reaction involving 13 steps. Meanwhile, this model gives the minimum deviations from calculations using the initial model (25 reactions), for the reaction times from 10^{-5} to $5 \cdot 10^{-3}$ s for all species, in particular for oxygen atoms. For comparison it may be noticed that for identification of the base mechanism in [56] only 16 steps similar to the range in Table 3.3 were considered. Therewith, according to calculations carried out in [51] step (8) included in the base mechanism is of low significance and is ranked as 16-th in the range. Meanwhile, steps (18) and (25) selected in the *value* analysis as rather weighty for the reaction, were not included in the base mechanism [56].

Now let us turn to the role in the descending order of steps (Table 3.5). In general this order as determined by the *value* method coincides with the data obtained from the sensitivity analysis method [28, 56]. Apparently, some observed differences are conditioned by the mismatch in the *value* characteristics and the sensitivity parameters, which determine the kinetic significance of steps. Here the following condition plays an important role: in the *value* analysis of a kinetic model the quality indicator of the reaction, the target functional, is clearly selected. This determines entirely the kinetic significance of steps. For example, the lesser difference (by the degree of importance) obtained by us for the similar steps (3) and (22) (the steps that result in chain initiation), as against those obtained in [56], seems to be more logical. One can make sure by comparing the rates of these steps. Also, the greater *value* contribution of step (3) as compared with that of step (22) may be explained. Thus, starting from the reaction time of $2 \cdot 10^{-3}$ s the rate of step (3) of the chain reaction autoinitiation exceeds the rate of the chain initiation by step (22).

Thus, by the example of the kinetic model for oxidation of formaldehyde in the presence of carbon oxide (II) it may be concluded that *value* analysis is a quite reliable method to reduce the reaction mechanisms that results in the identification of the base kinetic model for a chemical transformation.

Table 3.4. The rank of derived value contributions in descending order of their absolute values at different reaction times

t, s	$1 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$1 \cdot 10^{-4}$	$1 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	$3 \cdot 10^{-3}$	$5 \cdot 10^{-3}$
	12 0.71	12 0.71	4 -0.54	1 -0.83	1 -0.83	1 -0.83	1 -0.83
	16 -0.69	16 -0.70	10 0.53	2 0.41	2 0.41	2 0.41	2 0.40
	4 0.12	4 $8.5 \cdot 10^{-2}$	9 0.52	10 0.39	10 0.39	10 0.39	10 0.39
	9 $-4.4 \cdot 10^{-2}$	9 $-3.2 \cdot 10^{-2}$	11 0.30	$22 \cdot 10^{-2}$ $4.5 \cdot 10^{-2}$	$3 \cdot 10^{-2}$ $3.2 \cdot 10^{-2}$	$3 \cdot 10^{-2}$ $4.3 \cdot 10^{-2}$	$3 \cdot 10^{-2}$ $5.9 \cdot 10^{-2}$
	11 $1.2 \cdot 10^{-2}$	11 $2.0 \cdot 10^{-2}$	13 -0.15	$4 \cdot 10^{-2}$ $-2.9 \cdot 10^{-2}$	$4 \cdot 10^{-2}$ $-3.0 \cdot 10^{-2}$	$4 \cdot 10^{-2}$ $-3.1 \cdot 10^{-2}$	$4 \cdot 10^{-2}$ $-3.2 \cdot 10^{-2}$
	13 $9.8 \cdot 10^{-3}$	13 $9.7 \cdot 10^{-3}$	12 $-9.4 \cdot 10^{-2}$	$9 \cdot 10^{-2}$ $2.5 \cdot 10^{-2}$	$9 \cdot 10^{-2}$ $2.6 \cdot 10^{-2}$	$9 \cdot 10^{-2}$ $2.6 \cdot 10^{-2}$	$9 \cdot 10^{-2}$ $2.7 \cdot 10^{-2}$
	22 $1.3 \cdot 10^{-3}$	14 $-4.7 \cdot 10^{-4}$	1 $-3.5 \cdot 10^{-2}$	$3 \cdot 10^{-2}$ $1.8 \cdot 10^{-2}$	$22 \cdot 10^{-2}$ $1.9 \cdot 10^{-2}$	$22 \cdot 10^{-2}$ $1.9 \cdot 10^{-2}$	$13 \cdot 10^{-2}$ $-1.7 \cdot 10^{-2}$
	1 $1.0 \cdot 10^{-3}$	1 $2.4 \cdot 10^{-4}$	2 $1.1 \cdot 10^{-2}$	$13 \cdot 10^{-2}$ $-1.5 \cdot 10^{-2}$	$13 \cdot 10^{-2}$ $-1.6 \cdot 10^{-2}$	$13 \cdot 10^{-2}$ $-1.6 \cdot 10^{-2}$	$11 \cdot 10^{-2}$ $-1.6 \cdot 10^{-2}$
	14 $-6.5 \cdot 10^{-4}$	3 $-2.3 \cdot 10^{-4}$	14 $6.7 \cdot 10^{-3}$	$11 \cdot 10^{-2}$ $-1.4 \cdot 10^{-2}$	$11 \cdot 10^{-2}$ $-1.5 \cdot 10^{-2}$	$11 \cdot 10^{-2}$ $-1.5 \cdot 10^{-2}$	$12 \cdot 10^{-3}$ $8.6 \cdot 10^{-3}$
	2 $-7.1 \cdot 10^{-5}$	22 $1.5 \cdot 10^{-4}$	22 $-3.7 \cdot 10^{-4}$	$12 \cdot 10^{-3}$ $7.6 \cdot 10^{-3}$	$12 \cdot 10^{-3}$ $8.0 \cdot 10^{-3}$	$12 \cdot 10^{-3}$ $8.2 \cdot 10^{-3}$	$22 \cdot 10^{-3}$ $3.9 \cdot 10^{-3}$
	3 $-6.2 \cdot 10^{-5}$	24 $1.1 \cdot 10^{-4}$	3 $2.9 \cdot 10^{-3}$	$14 \cdot 10^{-4}$ $6.5 \cdot 10^{-4}$	$14 \cdot 10^{-4}$ $6.6 \cdot 10^{-4}$	$8 \cdot 10^{-4}$ $8.1 \cdot 10^{-4}$	$8 \cdot 10^{-4}$ $2.1 \cdot 10^{-3}$
	24 $-1.8 \cdot 10^{-5}$	2 $5.1 \cdot 10^{-5}$	16 $-4.8 \cdot 10^{-4}$	$16 \cdot 10^{-4}$ $-2.5 \cdot 10^{-4}$	$8 \cdot 10^{-4}$ $4.4 \cdot 10^{-4}$	$14 \cdot 10^{-4}$ $6.6 \cdot 10^{-4}$	$14 \cdot 10^{-4}$ $6.5 \cdot 10^{-4}$
Step numbers and adduced value contributions of steps	-	-	24 $-3.4 \cdot 10^{-5}$	8 $1.8 \cdot 10^{-4}$	16 $-2.7 \cdot 10^{-4}$	16 $-2.8 \cdot 10^{-4}$	25 $4.6 \cdot 10^{-4}$
	-	-	25 $-3.3 \cdot 10^{-5}$	25 $-3.7 \cdot 10^{-5}$	25 $-9.3 \cdot 10^{-5}$	25 $-1.8 \cdot 10^{-4}$	16 $2.9 \cdot 10^{-4}$
	-	-	8 $4.8 \cdot 10^{-6}$	6 $1.4 \cdot 10^{-5}$	6 $2.5 \cdot 10^{-5}$	18 $-4.3 \cdot 10^{-5}$	18 $1.6 \cdot 10^{-4}$
	-	-	-	18 $-4.0 \cdot 10^{-6}$	18 $-1.7 \cdot 10^{-5}$	6 $3.3 \cdot 10^{-5}$	6 $7.0 \cdot 10^{-5}$

Table 3.5. Comparison of series from step numbers ranked in the descending order, obtained by different methods, including the base mechanism

Analysis method	Number of steps															
	1	2	10	4	3	9	13	12	11	22	16	8	14	6	25	18
Value analysis [7,10]	1	22	3	2	9	4	8	12	11	1	-	-	-	-	-	-
Sensitivity analysis[69]	10															
Principal components analysis [56]	22	10	4	9	2	16	12	11	1	13	14	3	6	7	24	8
Base (minimal) reaction model[28,56]	1	2	3	4	6	8	9	10	11	12	13	16	22	-	-	-

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Chapter 4

VALUE ANALYSIS AS A BASIS TO PURPOSELY INFLUENCE ON MULTISTEP CHEMICAL REACTIONS

The *value*-based approach significantly improves the effectiveness of procedures of controlling chemical reactions. Optimal control on the basis of the *value* method is widely used with Pontryagin's Maximum Principle, while simultaneously calculating the dynamics of the *value* contributions of individual steps and species in a reaction kinetic model. At the same time, other methods of optimal control are briefly summarized for: a) calculus of variation, b) dynamic programming, and c) nonlinear mathematical programming.

The *value* approach allows to solve one of the most important questions in the theory of optimal control, namely, to make chemically meaningful choice of the most effective control parameters. Simultaneously, the physical-chemical, *value*-based understanding of basic mathematical concepts of the Maximum Principle makes possible to determine their initial magnitudes. This greatly simplifies the computational procedures and makes them effective.

The *value* method is also successfully used to control empirically the chemical reactions, even in the case when information on reaction mechanism is limited. In order to make full use of the available information on the reaction mechanism, the reaction system is represented as a flow graphs. In flow graphs the key species of the reaction and the direction of chemical transformations between them are highlighted. Quantitative empirical parameters characterizing the effective rate constants for conversions are determined by the methods of mathematical statistics, comparing the empirical mathematical model with experimental results. Next, using a *value* approach the most effective control parameters are revealed and their optimal trajectory is determined according to the selected functional of a target reaction.

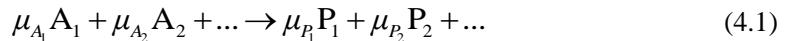
The *value* approach also allows solving successfully the problem of non-empirical determination of the effective stimulator (the catalyst, initiator, and promoter) and the inhibitor of a complex reaction in a series of similar compounds. In this approach it is crucial that the reactivity indices of molecular structure of stimulators and inhibitors are represented as control parameters of the reaction system.

In general, it is concluded that the *value* quantities arising from the control ideology, adequately describe the kinetic significance of species of the constituents of a reaction system according to the target characteristics of the reaction. The objective character of *value* concepts in chemical kinetics is also supported by analogy with the classical canonical description of the behavior of dynamic systems.

4.1. SELECTIVITY, CONVERSION, AND PRODUCT YIELD OF CHEMICAL REACTIONS

The selectivity, conversion, and product yield of chemical reactions along with the power inputs, basically determine the practical availability of a chemical process. Definitions of these parameters may be found in [1-6].

A chemical reaction is presented in the form:



where A_i , P_i are the initial substances and reaction products, respectively, μ_{Ai} and μ_{Pi} are the stoichiometric coefficients of the reaction.

Integral selectivity by the product P is defined as

$$S = f \cdot [P] / \Delta[A], \quad (4.2)$$

where $f = \mu_A / \mu_P$ is the normalizing factor, $\Delta[A] = [A]_0 - [A]_t$, $[A]_0$ and $[A]_t$ denote the initial and current concentrations for the substance A , respectively.

The dependence of S on the rates of consumption of the substance $A(r_A)$ and the accumulation of the product $P(r_P)$ is presented by the expression:

$$S(t) = f \cdot \left\langle \int_0^t r_p(t) dt \right\rangle / \left\langle \int_0^t r_A(t) dt \right\rangle. \quad (4.3)$$

Conversion is the degree of chemical transformation of the initial substance

$$K_A = \Delta[A] / [A]_0 = - \left\langle \int_{[A]_0}^{[A]} d[A] \right\rangle / [A]_0 = \left\langle \int_0^t r_A dt \right\rangle / [A]_0. \quad (4.4)$$

The *yield of the product P* is expressed through its portion relative to the initial concentration A

$$\varphi_r = f \cdot [P] / [A]_0 = f \cdot \left\langle \int_0^P d[P] \right\rangle / [A]_0 = f \cdot \left\langle \int_0^t r_p dt \right\rangle / [A]_0. \quad (4.5)$$

Using expressions (4.2), (4.4) and (4.5) we find:

$$\phi_r = S \cdot K. \quad (4.6)$$

For the selectivity, the conversion, and the product yield 0 and 1 are the limiting values.

In [1-6] the *differential selectivity* is defined as the “instant” selectivity of a reaction at a given time t :

$$S_d = -\frac{f \cdot d[P]}{d[A]} = \frac{f \cdot r_p}{r_A}. \quad (4.7)$$

The link between the integral and differential selectivities is determined by the following [1]:

$$S = \frac{1}{K} \int_0^K S_d dK. \quad (4.8)$$

Expressions (4.3)–(4.5) in which dependences for performance criteria of a chemical process on its rate characteristics are given, emphasize the important idea pronounced by N.M. Emanuel [1] that chemical kinetics is the scientific basis of chemical technology. Note that expressions for efficiency parameters of chemical reactions frequently do not permit *per se* to offer specific ways to achieve the maximum output from a chemical process. Realization of this problem is one of main objectives of the *value* approach, the underlying principles of which are expounded in the next chapters.

4.2. INFORMATION ON THE SOLUTION METHODS FOR OPTIMAL CONTROL OF CHEMICAL PROCESSES

The opportunity of choosing ways to efficiently influence the course of complex chemical reactions may be considered as one of the advantages of the *value* approach. In this section a brief review is given on the mathematical methods for solving tasks of the *optimal control*, where efficient influencing is conditioned in many respects by the successful selection of control parameters. Here we cite only the general approaches, but not the details of specific methods on optimal control. For readers interested to get detailed knowledge regarding the various aspects of mathematical methods for optimal control, a number of excellent monographs [7-25] devoted to this matter are recommended.

Firstly, among the tasks on optimal control of chemical processes is the finding of optimum conditions for the reactions leading to the high yield and quality of the target product, together with the minimum number of side products. The development of effective chemical-engineering schemes includes the choice of optimum versions in the instrumental design of chemical processes, designing optimum chemical reactors [4,5,7,8,15,16], and others related to this class of tasks. At the same time technical and economic indices of the processes are of vital importance.

The choice of such a regime in the change of control parameters, providing the best path for the conversion of a reaction system to the selected end, is understood as optimal control. In other words, from all possible versions of changes in parameters, the single (optimal) one is selected, which leads to the desired result.

Physicochemical characteristics of reactions (pressure, temperature, concentration of reagents, catalysts, etc.) together with the characteristics of the technological scheme, become the control parameters of chemical processes, accepted in the engineering practice. Usually the control parameters, like any parameter of a chemical process, may be varied in a certain range. Limitations in the temperature, pressure, and concentrations of initial and final substances, together with the technical requirements of explosion safety and ecological compatibility of the realized reaction may be offered as proof of illustrations.

The solution of task on the optimal control becomes possible if internal connections for the process under study are formalized, i.e. if a mathematical model for the controlled system exists in the form of a system of differential equations. In this case kinetic equations for the species of a reaction system frequently act as such a model.

The solution of the task on optimal control is obtained mainly by the following stages:

1. Selection of the target, optimality criterion.
2. Mathematical modeling of the process.
3. Selection of control parameters.
4. Finding the regime of optimal control.

Mathematically, the problem of optimal control can be formulated as follows.

We have:

- The state equations representing a system of ordinary differential equations

$$\frac{d\mathbf{x}(t)}{dt} = f[\mathbf{x}(t), \mathbf{u}(t)], \quad (4.9)$$

where $\mathbf{x}(t)$ is a m -dimensional vector specifying the system state (*phase variables*) and $\mathbf{u}(t)$ is the r -dimensional vector of *control variables*.

- Boundary conditions for phase variables at the initial (t_0) and final (t_f) times:
 $\mathbf{x}(t_0) = \mathbf{x}^0$, $\mathbf{x}(t_f) \in S$, where S denotes a hypersurface of the phase variables.
- The system of restrictions imposed on phase variables $\mathbf{x}(t)$, $\mathbf{u}(t)$.
For which we need:
- To identify the dynamics of the allowable controls so that the target functional or, otherwise the quality index of the process attains the maximum or minimum quantity.

In the majority of cases the quality index of the system is presented in the following form:

$$I(t) = \int_{t_0}^{t_f} F[\mathbf{x}(t), \mathbf{u}(t)] dt. \quad (4.10)$$

For instance, if we are interested in the high yield of a certain product P_i at a time t_f , then the optimality criterion may be presented in the following way:

$$I(t) = \Delta[P_i(t)] = \int_{t_0}^{t_f} r_{P_i}[\mathbf{x}(t), \mathbf{u}(t)] dt \rightarrow \max, \quad (4.11)$$

where r_{P_i} is the rate of product formation P_i .

To solve the assigned mathematical problem for optimal control, certain methods are used as briefly described below.

Calculus of variation. Solution of the problem on optimal control is found through the variation of the basic variables of the target functional, equating them to zero and solving the system of equations [9,19,21].

Let us use the target functional that specifies the chemical process

$$I(t) = \int_{t_0}^{t_f} F[y_1(t), \dots, y_n(t), \dot{y}_1(t), \dots, \dot{y}_n(t)] dt. \quad (4.12)$$

The extremality of this functional fits to the condition

$$\delta I = 0, \quad (4.13)$$

where δI is the variation of I by functions $y_i(t)$ and $\dot{y}_i(t)$.

Condition (4.13) leads to the well-known Euler's equations

$$\frac{d}{dt} \left(\frac{\partial F}{\partial \dot{y}_i} \right) - \frac{\partial F}{\partial y_i} = 0, \quad i = 1, 2, \dots, n. \quad (4.14)$$

The solution of Euler's equations with boundary conditions $y(t_0) = y_0$ and $y(t_f) = y_f$ enables determining the form of the function $y(t)$ whereby the target functional possesses the extremum value. If a meaning of control parameters is imparted to \dot{y}_i , i.e. $\dot{y}_i \equiv u_i(t)$, then a retrieval of extremum values for the target functional (4.12) is defined as a task of optimal control in its traditional interpretation.

In case when additional conditions should be taken into account, the Lagrange multipliers are applied as coupling equations.

The coupling equation is presented in the following way:

$$\varphi_j(y_1, \dots, y_n(t)) = 0 \quad (j = 1, 2, \dots, m) \quad m < n \quad (4.15)$$

The functions $y_1(t), \dots, y_n(t)$, obeying the coupling conditions through Lagrange multipliers $\lambda_i(t)$ may be derived from the system of Euler-Lagrange differential equations

$$\frac{d}{dt} \left(\frac{\partial \Phi}{\partial \dot{y}_i} \right) - \frac{\partial \Phi}{\partial y_i} = 0, \quad i = 1, 2, \dots, n, \quad (4.16)$$

where $\Phi \equiv F + \sum_{j=1}^m \lambda_j(t) \varphi_j$.

Imposing restrictions on the phase variables and control parameters is one of the difficulties arising when the Euler-Lagrange equations are applied. This case is frequently met in the optimal control of chemical processes. The Euler-Lagrange method enables to calculate the extremum of the target functional in the so-called classic version when the function $y(t)$ has no limitations. However, the extremum often is not located in the points where derivatives or variations become zero, but on the boundary of the acceptable region of control parameters and phase variables.

Moreover, quite often are the cases when the derivatives of functions and functionals in specific points and regions do not really exist (e.g. in discontinuous or broken-line functions). To get over these difficulties, non-classic methods of calculus of variations are applied. Among these the most effective and naturally the more popular ones are Bellman's method of dynamic programming and Pontryagin's principle of maximum.

Bellman's method of dynamic programming. Dynamic programming formulated by Bellman [12] as *the optimality principle* is based on V.H. Hambartsumyan's *principle of invariant insertion* [26]. The latter is stated as follows: each section of an optimal trajectory is also an optimal trajectory. At first sight, such a simple statement permits to solve in an "elegant" way the complicated mathematical problem on optimal control. The optimality principle makes it possible to isolate an infinitely small section from the variation interval of the argument and to solve the problem for this interval. Then the obtained solution can be generalized for arbitrary variation of the argument. It should be noted that applying the method of dynamic programming allows the solution of optimization problem to be reduced to the solution of the well-known Hamilton-Jacobi equation [12].

For simplest cases the use of the dynamic programming method leads to analytical solutions. Meanwhile, for several phase variables and control parameters the search of optimal solutions is an extraordinarily complicated problem. Therefore, the application of the method of dynamic programming proves to be accurate in numerical computations where powerful computer techniques are used.

Nonlinear mathematical programming. For a wide variety of problems concerning the optimal control of chemical-engineering processes, the mathematical programming (exploratory methods) is the most routine tool to obtain numerical solutions [13,16-20,24,25]. In contrast to the classical optimization theory, in mathematical programming special

attention is focused on the tasks in which restrictions imposed on the variation area of variables strongly influence the solution.

Mathematical programming is ranked as *linear* and *nonlinear* depending on the type of target functional and restriction system is used for the control parameters and phase variables. The problems of optimal control of chemical processes generally belong to the class of nonlinear mathematical programming. The term “programming” is embodied in the solution technique for finding the extremum of a target function or functional. Such methods are specified as the programs for searching solutions of the extremality of a problem. The general scheme for the solution of mathematical programming of a problem is as follows: the area of permissible values for the arguments of a target functional is defined, followed by the recurring search steps, so that each step includes the checking of the solution and its improvement until an optimum solution is achieved.

Thus, finding the extremum of the function $I=f(x_1, x_2, \dots, x_m)$ in general, comes to the following. In the permissible space of the variables of $I=f(x_1, x_2, \dots, x_m)$ a certain point $f^0(x_1^0, x_2^0, \dots, x_m^0)$ is selected as the zeroth approximation. Further, when an extremum is found in the form of a maximum, search is made to find $f^1(x_1^1, x_2^1, \dots, x_m^1)$ that meets the condition $f^1 > f^0$. The same procedure is repeated now from the starting point $f^1(x_1^1, x_2^1, \dots, x_m^1)$ and so on. The search is stopped when the following condition is satisfied:

$$\Delta f_i / \Delta x_i \leq \varepsilon ,$$

where $\Delta f_i = f(x_1 + \Delta x_1, \dots, x_i + \Delta x_i, \dots, x_m + \Delta x_m) - f(x_1, \dots, x_i, \dots, x_m)$, Δx_i and ε as small quantities.

Certainly, determination of the function's extremum is dependent on the chosen step size Δx_i , while duration and efficiency of the problem's solution depend also on the selected direction of the search steps. Nonlinear mathematical programming covers a wide variety of problems for which general numerical solution methods are not available. A lot of publications are devoted to this issue (see, for example, [13,17-19]). For this reason we will mention only the general aspects.

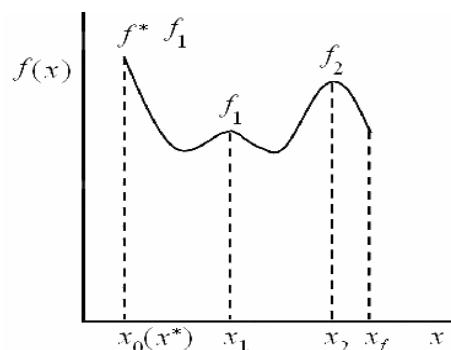


Figure 4.1. Global (f^*) and local (f_1, f_2) maxima of the function $f(x)$.

The methods of non-linear mathematical modeling are divided to those of *random* and *directed* searches, based on the organization of the searching process. According to another classification, the methods of nonlinear mathematical programming may be divided into *local* and *global* ones. Thus, some methods (for example, the widely used gradient method) ensure only the finding of the local extremum (Figure 4.1). Researchers have in their disposal a number of methods enabling to define the global (absolute) extremum for the target functional or function. Surely these concepts may be presented in quantitative form.

Pontryagin principle of maximum. The totality of results obtained in 1951-1961 by the group of mathematicians led by L.S. Pontryagin [9,14,22] serves as a basis for the theory of maximum (historical name).

The principle of maximum at given mathematical conditions determines the optimal control by means of the sequential time selection of the control from the specified class of the controlling operations.

Let us have a system described by the equations

$$\frac{d\mathbf{x}(t)}{dt} = f[\mathbf{x}(t), \mathbf{u}(t)], \quad (4.17)$$

where $\mathbf{x} = (x_1, x_2, \dots, x_m)$ with the boundary conditions $x_i(t_0) = x_i^0$; $x_i(t_f) = x_i^f$, $\mathbf{u}(t)$ are control variables.

In this case it is assumed that t_f , and accordingly $x_i(t_f)$ are fixed. It is necessary to determine the permissible controlling $\mathbf{u}(t)$ that maximizes or minimizes the quality indicator of the process

$$I(t) = \int_{t_0}^{t_f} F[\mathbf{x}(t), \mathbf{u}(t)] dt. \quad (4.18)$$

The control vector obeys some restriction: $\mathbf{u}(t) \in \mathbf{U}$.

In the theory of Pontryagin's maximum, functions $\psi_i(t)$ are used conjugate to x_i . The conjugate functions ψ_i are determined by differential equations

$$\frac{d\psi_i}{dt} = - \sum_{k=0}^m \frac{\partial f_k}{\partial x_i} \psi_i, \quad (4.19)$$

where $f_0 \equiv F[\mathbf{x}(t), \mathbf{u}(t)]$.

Hamilton's function is also introduced in the following way:

$$H(\mathbf{x}, \boldsymbol{\psi}, \mathbf{u}) = \psi_0 F(\mathbf{x}, \mathbf{u}) + \sum_{i=1}^m \psi_i(t) f_i(\mathbf{x}, \mathbf{u}) \quad (4.20)$$

Using Hamilton's function and equations (4.17), (4.19) may be written in a suitable kinetic form

$$\begin{cases} \frac{dx_i}{dt} = \frac{\partial H}{\partial \psi_i}, & \text{(state equations)}, \\ \frac{d\psi_i}{dt} = -\frac{\partial H}{\partial x_i}, & \text{(conjugate equations)} \end{cases} \quad (4.21)$$

where $i = 1, 2, \dots, m$.

The principle of maximum states that if $\mathbf{u}^*(t)$ is the optimal control, then there exists a continuous non-zero m -dimensional vector, a function $\psi(t) = [\psi_1(t), \dots, \psi_m(t)]$, which satisfies the system of equations (4.21) and the condition $\psi_0 = \pm 1$ depending on either a maximum or a minimum problem is solved. Simultaneously, the Hamiltonian defined by (4.20) as a function of the variable $\mathbf{u}(t)$ reaches the maximum value on the optimal trajectory, namely

$$H[\mathbf{x}^*(t), \psi^*(t), \mathbf{u}^*(t)] = \sup_{\mathbf{u}} H[\mathbf{x}(t), \psi(t), \mathbf{u}(t)] = \text{const}, \quad (4.22)$$

where $\mathbf{u}^*(t)$ is the optimal control, and $\mathbf{x}^*(t)$ is the optimal trajectory determined by the condition. If the final time is free, then:

$$\sup_{\mathbf{u}(t) \in \mathbf{U}} H = 0, \quad (4.23)$$

The principle of maximum leads to the following strategy for solving the optimization problem:

- First, the system (4.21) involving $2m$ differential equations is solved at specified \mathbf{u} values and the variational dynamics for $x_i(t)$ and $\psi_i(t)$ are calculated.
- Then the analysis of the Hamiltonian H , as a function of the variable $\mathbf{u}(t)$ starts

$$H = H[\mathbf{u}(t)]. \quad (4.24)$$

Simultaneously the system of equations (4.21) is solved to determine the $\mathbf{x}(t)$, $\psi(t)$ values, as well as Hamiltonian H according to (4.20).

- In the final stage the controlling is chosen that maximizes the Hamiltonian function. It should be specified that values for $\mathbf{u}(t)$ are selected from certain types of the optimal control $\mathbf{u}^*(t) : \mathbf{u}^{\text{lm}}, \mathbf{u}^{\text{c}}, \mathbf{u}^{\text{cl}}$. Here \mathbf{u}^{cl} is the classical type of controlling determined from the condition $\delta H / \delta \mathbf{u} = 0$; \mathbf{u}^{c} is the controlling related to

restrictions imposed on phase variables, and \mathbf{u}^{lm} is the controlling taking into account restrictions imposed on control parameters. The types of controlling are examined over the whole process.

As may be seen, the maximum principle does not determine optimal control immediately and requires proper assembling from the mentioned controlling types. This does not complicate the calculational process of the optimal control markedly, and sorting out the options represents usually a relatively simple task. More important is the analysis of the Hamiltonian H , which is some kind of an “indicator” for the correctness in the selection of a certain variety of control options, and enables to feel deeply the structure of control.

We note one more important aspect of using the calculus of variations, including the principle of maximum. This is associated with the definition of boundary conditions which, in turn, is necessary to solve the system of differential equations (4.21). In problems on the optimal control frequently the values of $\mathbf{x} = \mathbf{x}(t_f)$ are not fixed. In this case the final values of the conjugate functions $\psi_i(t_f)$ must be established exactly.

The values of $\psi_i(t_f)$ are determined from a strictly observed rule called the *transversability condition*. So, for example, if the edge values $x_i(t_f) = x_i^f$ at $i = 1, 2, \dots, m$, are known, then according to the transversability condition the following boundary values fit to the conjugate functions:

$$\psi_i(t_f) = 0, \quad i = m' + 1, \dots, m,$$

The transversability condition makes it possible also to determine $\psi_i(t_f)$ values for boundary conditions at which the x_i^f edge values are in a mutual functional dependency. Nevertheless, it appears that the initial conditions for the state equation are determined on the left side, i.e. at the initial time, while proper equations of conjugate functions are on the right side, i.e. at the final time. This creates some problems in the numerical solution of the system of equations (4.21). As usual this difficulty is overcome by using the method of successive approximations. The schematic procedure is as follows: starting from some $\psi_i(t_0)$ value and solving the system of equations (4.21), a value for $\psi_i(t_f)$ is calculated. Thus, the $\psi_i(t_0)$ is selected so that it results in or approximates the $\psi_i(t_f)$ calculated from the transversability condition. Naturally, this calculation procedure is conducted using special algorithms, frequently by methods of nonlinear mathematical programming. But then it is necessary to overcome the problem of iterative convergence.

Solution of the optimization problem is simplified markedly if the initial value of $\psi_i(t_0)$ is guessed at once. Usually this becomes possible if one succeeds in determining the “physical, kinetic” meaning of the conjugate function ψ_i for the dynamic system under consideration and for the specified problem. This question will be elucidated in Section 4.3.

4.2.1. Conclusion

As may be imagined from the above, chemists and chemical engineers have at their disposal a wide set of methods to solve the problem of optimal controls. Meanwhile, by now there is a lack of comprehensive methods to meet fully the requirements of researchers in solving the optimization problems. Choosing one or another method they usually are guided by the type of problem solution, by the preconditions imposed on the process variables, calculation times, etc. At the same time it is quite a complicated task to offer ready for use recommendations. Much depends on the creative work of a researcher. Therefore, we consider it appropriate to give in the conclusion of this Section the general characteristics of the methods for optimal control and to touch upon some of the problems faced by researchers when using the described theoretical methods.

Classical methods of calculus of variations are attractive from the point of view of the opportunity to obtain solutions in analytical form. But this is feasible in simple cases, which often are far from the demands of the state-of-art practice. In complicated cases, at a large number of optimization parameters, numerical approaches are used to solve the appropriate Euler-Lagrange equations. The main obstacle arising here is related to the fact that the numerical solution of the system of differential equations may turn out to be more complicated than the solution from the very beginning of the optimization problem by numerical methods of mathematical programming.

It should be emphasized once again the important point confining considerably the application field of the calculus of variations. When determining extrema of the target functional the Euler-Lagrange method does not take into account the possibility for the existence of limitations imposed on the control parameters and phase coordinates.

Meanwhile, as it was mentioned above, when solving the problems of optimal control for the chemical processes, it is rather common that a system reaches its optimal value just on the boundaries of the admitted range of variables of the target functional.

These difficulties may be overcome using the methods of nonlinear mathematical programming. They are very promising from the computational standpoint. One can not ignore the fact that nonlinear mathematical programming is relevant also when applying other methods of the optimal control. On the contrary, one can make sure easily in the inevitability of nonlinear mathematical programming, except for the most simple cases. Then, the selection of nonlinear programming requires ample ingenuity.

Despite the obvious success of numerical methods for nonlinear mathematical programming, their weaknesses were discovered early on. Among them it should be highlighted the main one, namely, the absence of the physicochemical visualization. To some extent it relates also to Bellmann's dynamic programming method. Naturally, incomplete information about the nature of the studied process on "a way" to optimal result constrains strongly the creative capabilities of a researcher. In particular, identification of the most active control parameters from a variety of the "candidates" is complicated, thus also complicating the solution of the defined problem.

In this respect Pontryagin's principle of maximum provides an exceptional opportunity. Its specific feature is to highlight the control structure in the appropriate Hamiltonian and to identify the effective control parameters. This allows to perceive the participation of controlling factors throughout the entire process. Further, we will try to make use of just this

advantage of the principle of maximum, with maximum benefit to identify the ways of the target-oriented influence on a chemical reaction from the viewpoint of the *value* approach.

At the same time the principle of maximum is not so universal when restrictions are imposed on the phase variables of the process. Some difficulties also arise at determining the initial values used in the method of conjugate functions $\psi_i(t)$, typical in the calculus of variations. Moreover, the nature of conjugate differential equations is such that they exhibit an excessive sensitivity to predetermined initial values $\psi_i(t_0)$. Nevertheless, when the principle of maximum is used, in many cases one can succeed in providing the necessary calculational accuracy and to cope with the task of optimal controlling.

4.3. THE VALUE METHOD OF ANALYSIS FOR SOLVING THE PROBLEM OF TARGETED INFLUENCE ON MULTISTEP CHEMICAL REACTIONS

As we have already mentioned, one of the most important problems of chemistry consists in raising the selectivity of chemical reactions at a high degree of conversion of initial substances and optimal reaction rates. This opens new perspectives for the chemical technology in creating high-performance chemical production with low emission and waste. The problem set in such a manner stimulates developing new approaches for *targeted influence on chemical processes*.

It should be emphasized here that the goal-directed influence implies a more wide range of issues than those discussed in optimal control. Let us try to explain this difference. As it follows from the material presented in this chapter, the problem of optimal control comes to the identification of the optimal trajectory for selected control parameters or parameters according to the available kinetic model and the assigned goal. And the goal-directed influence apart from optimal control implies efficient approaches on the *intelligent chemical influence on reactions*, for instance through active additives (catalyst, inhibitor, initiator, and so on), variations in the reaction medium, the molecular structure of species of the reaction system, etc.

Development of theoretical principles of goal-directed influence on a complex chemical process, similar to the described cases of optimal control, is based on the detailed mechanism of the process. Such an approach is the most fundamental with a relatively wide prognostic range. Hence, the principles of goal-directed influence do not interpret the reaction mechanism passively, but allow also correcting the ideas on the mechanisms, making them more realistic. Here a quite simple principle is applicable: if the kinetic model is accurate and reliable, then it has heuristic capabilities, that is, it describes correctly the behavior of a reaction system when varying the conditions of the reaction.

The abovementioned enables us to relate the approaches of goal-directed influence on chemical processes to one of the most important steps of kinetic examination, which from general points of view comes to the following scheme (Figure 4.2):

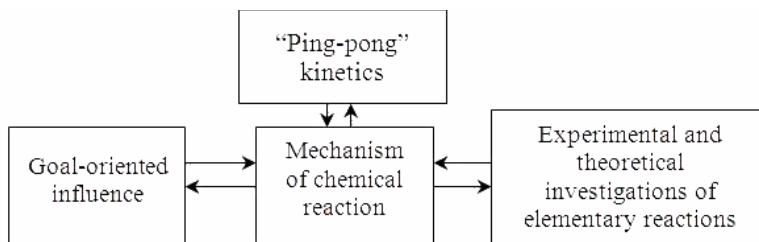


Figure 4.2. Formalized scheme of the approaches for the investigation of multistep chemical reactions.

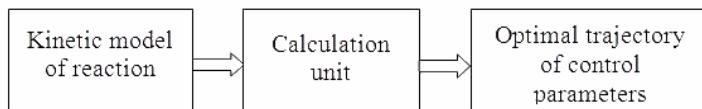


Figure 4.3. Main stages in the optimal control of chemical reactions.

Now, let us return to the methodology of applying the theoretical methods for optimal control briefly described earlier in Chapter 4.2.

Common to these methods is that the reaction kinetic model with few exceptions is perceived as the calculating basis for finding the optimal trajectories for control parameters as follows:

Some features of this scheme restrict its more wide application. The most fundamental is that such a sequence of operations does not disclose the role of individual steps and species of the kinetic model. Absence of chemical obviousness in the calculation unit complicates the very process on the selection of the priority of the influence on chemical reaction, therewith it does not permit to refer to the structure of molecules and the chemistry of their conversion.

As a consequence of the mentioned feature, the difficulties arise when the foregoing approaches of goal-directed influence on chemical process are used fully. Thus, the chemical effect of “active” influencing factors (catalyst, inhibitor, initiator, reaction medium, etc.) is realized through their participation in individual steps of the chemical process. Controlling methods, which do not reveal the role of individual steps and species, virtually are not able to support a researcher in the correct choice of such “active” factors for the chemical process.

Thus, our main conclusion is as follows: the calculation unit presented in the scheme (Figure 4.3) must be filled by chemical meaning, resulting in the identification of the role of species and steps in the kinetic model. Just this principle lies in the basis of the *value* approach of goal-directed influence on chemical systems and is discussed in this chapter [27-29].

In general terms the sequence of the *value* principle’s application in the control of multistep chemical reactions may be presented by the following scheme:

Let us emphasize once more that, in contrast to the diagram presented in Figure 4.3, the procedures mentioned in Figure 4.4, enable to carry out more meaningfully from the chemical point of view the control of a multisteps chemical reaction.

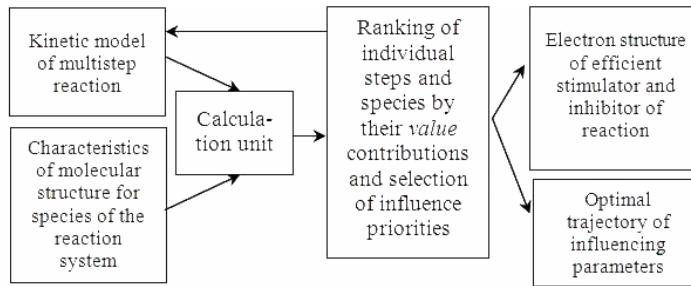


Figure 4.4. Sequence of stages at using the *value* approach for chemical reaction controlling.

4.3.1. Defining the Optimal Values for Controlling Parameters by Means of the *Value* Analysis of the Kinetic Model

The principle of Pontryagin maximum (described in Section 4.2) lies in the basis of the *value* approach at optimal control, resulting in the identification of *value* contributions of species and individual steps of the kinetic model.

When solving the problem on controlling the chemical reaction, the spatially homogeneous chemical system under isothermal conditions is described by a set of ordinary differential equations. Unlike equation (3.1), in the following system of kinetic equations the control parameters $\mathbf{u}(t)$ are separated

$$\frac{dc_i}{dt} = f_i(\mathbf{c}, \mathbf{k}, \mathbf{u}), \quad i = 1, 2, \dots, m, \quad (4.25)$$

where $\mathbf{c}(t)$ is an m -dimensional vector of species concentrations with $\mathbf{c}(t_0) = \mathbf{c}^0$, \mathbf{k} is an n -dimensional vector of rate constants for individual steps, and \mathbf{u} is a r -dimensional vector of control parameters.

$\mathbf{u}(t)$ is assumed to be changed in the range

$$\mathbf{u}(t) \in \mathbf{U}. \quad (4.26)$$

To specify the regime of the optimal control let us write the canonical equations as in the preceding Section [9,14], fitting to the target condition:

$$I(t) = \int_0^t F(t) dt = \text{extremum}, \quad (4.27)$$

$$\begin{cases} \frac{dc_i}{dt} = \frac{\partial H}{\partial \psi_i} = f_i \\ \frac{\partial \psi_i}{dt} = -\frac{\partial H}{\partial c_i}, \quad i = 1, 2, \dots, m \end{cases} \quad (4.28)$$

where H is the Hamiltonian of the system

$$H = \psi_0 F + \sum_{i=1}^m \psi_i f_i , \quad (4.29)$$

$\psi_0 = \pm 1$ when solving the problem with regard to the maximum or minimum, respectively.

Let us move to the procedure of finding the optimal controlling regime with simultaneously defining the *value* parameters.

We remind the statement of Pontryagin principle of maximum: the Hamiltonian calculated on the basis of the system of equations (4.28) and equation (4.29) as a function of the variable $\mathbf{u}(t)$ at optimal controlling $\mathbf{u}^*(t)$, reaches its maximum value

$$H\left(\mathbf{u}^*\right) = \sup_{\mathbf{u}} H = 0 . \quad (4.30)$$

From (4.29) and (4.30) we obtain an equation describing the dynamics of output parameter $F(t)$ under the condition of minimum for the corresponding target functional ($I(t)$) [27-29]

$$F(t) = \sum_{i=1}^m \psi_i(t) f_i(t) = \sum_{i=1}^m b_i(t) = \sum_{j=1}^n G_j(t) r_j(t) = \sum_{j=1}^n h_j(t) , \quad (4.31)$$

where n and m denote the number of individual steps and the chemical species (the initial and intermediate) of the reaction mechanism, respectively.

Analysing expression (4.31) one can conclude that both the conjugate function $\psi_i(t)$, and the $G_j(t)$ define exactly the *values* of a species and an individual step under the optimal reaction mode, according to the definition presented in Chapter 3.

In particular, it follows from the given equation that the sum of *value* contributions for steps $h_j(t)$, and species $b_i(t)$, is equal to the quantity of the selected output parameter $F(t)$ of the chemical reaction. This illustrates again the objectivity and physicochemical interpretability at describing the role of species and individual steps via the *value* parameters.

Let us highlight again that determination of the *value* contributions for the species and steps of the kinetic model improves considerably the efficiency of solving the problem of optimal control. This consists of the following:

- *Value parameters enable to solve one of important problems in the theory of optimal control, namely to perform the preliminary selection among the tools of impact on a chemical process.* It is easy to select the most effective and feasible control parameter, considering the time behavior of *value* contributions for the species and individual steps for several values of $\mathbf{u}(t)$ from the interval (4.26). In this case the control parameter acts intensively on the reaction through influencing the rate of the j -th step or the accumulation rate of the i -th species having ponderable contributions.

In case when the control parameter influences simultaneously on the several steps of a complex chemical process, the positive or negative effect on the target functional is determined by the sum of the *value* contributions for these steps.

- Besides, as is already known (see Section 3.4) *the value analysis of the kinetic model promotes increasing its prognostic capability*, thus broadening possible interval of the adequate effect of the control parameter $\mathbf{u}(t)$ (equation 4.26).

It should be reminded what are further steps away from finding the optimal trajectory of the control parameter $\mathbf{u}^*(t)$, from the viewpoint of the Pontryagin principle of optimality.

Solution of the system of equations (4.28) corresponds to the optimal trajectory $\mathbf{u}(t)$ provided that conditions (4.26) and (4.30) are met, and the optimum value $\mathbf{u}^*(t)$ is selected from the values \mathbf{u}^{lm} and \mathbf{u}^{cl} .

The control parameters influencing the rates of individual steps of a complex reaction more often represent the species' concentrations participating in these steps or the concentration of the activator (e.g., catalyst) that changes the rates of steps. Usually the step rates depend linearly on the mentioned parameters. If it is not the case, it is practical to specify the target functional (the quality indicator of the reaction) in such a manner that results in the linear dependence of the Hamiltonian on the control parameter. The new "linear" target functional is selected from a set of functionals with the same extreme values, which specify the selected target

$$H = g_0 + g_i u . \quad (4.32)$$

Namely, owing to the linearity of equation (4.32) the $u(t)$ value that corresponds to the optimal control and simultaneously maximizes the Hamiltonian function is determined by the limit values of the control variable.

In fact, the linear dependence of the Hamiltonian function on $u(t)$ excludes from discussing the classical controlling condition $\partial H / \partial u$. This is conditioned by the fact that such a dependence comes to the condition $g_i = 0$, i.e. there is no sensitivity with respect to the control parameter. The condition $g_i = 0$ in this case specifies a point of change in the control parameter from u^{max} to u^{min} and *vice versa* (Figure 4.5) [14].

Structuring the Hamiltonian by the *value* contributions of steps allows to realize an easy selection between the boundary values of the control parameter. As shown in Figure 4.5, u^{max} corresponds to the positive $g_i(t)$ in equation (4.32), and u^{min} to the negative $g_i(t)$. If the control parameter influences an individual step, then during the selection of the controlling type, one can be guided by the sign of the *value* for this step.

At an heterogeneous reaction system changeover of the control parameter may be carried out, for example, by introducing a reaction species or by its removal from the reaction sphere. For homogeneous systems another controlling strategy may be chosen, that is to regulate the supply rate of the proper reaction species into the reaction mixture, through which the control is realized.

Let us again appeal to the question on the usefulness of the information about the kinetic trajectories of the *value* parameters, fitting the optimal regime of a chemical process. Based on these data, that actually contain information about the role of steps and reaction species, one can recommend new conditions for the reaction (e.g., change the reaction medium by introducing a new reagent and so on); in other words, to solve such an important problem of chemistry and chemical technology as a *modernization of chemical processes*.

Now let us return to the integration problem of a system of conjugate differential equations. As mentioned in the preceding Section, when solving the problems with the use of the calculus of variations, usually there is a need to overcome the difficulties associated with finding the initial $\psi_i(t_0)$ values.

As already mentioned, for this, it is accepted to resort to the transversality condition and to determine the ψ_i value at the final time t_f . Further, by the method of successive approximations (iteration procedure), the initial $\psi_i(t_0)$ values are determined that correspond to the predetermined ψ_i values at the final time t_f [9,14].

Meanwhile, accentuating on the “physical, kinetic” meaning of the reaction species’ *value* $\psi_i(t_0)$, and an apt selection of the target functional, make it possible to overcome the above-mentioned difficulty and predict the $\psi_i(t_0)$ values. Definition of the boundary conditions for the set of equations (4.28) just at the start of the process provides an opportunity to avoid the solution of problems of convergence and the accuracy of iterative procedures. It should be reminded (see Chapter 3) that selection of the function type for output parameter of the target functional is also conditioned by the possibility of determining the initial values of $\psi_i(t_0)$, starting from their physicochemical, kinetic meaning. Examples on the determination of the initial $\psi_i(t_0)$ values proceeding from physicochemical, kinetic meaning were illustrated in Chapter 3 and will be shown further in Chapters 5-7.

Demonstration of the optimal control of chemical reactions with preliminary *value* rating of the individual steps of the kinetic model is presented in Chapter 6.

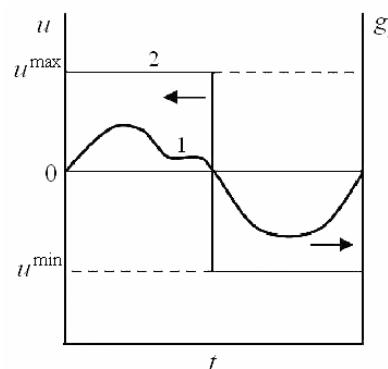


Figure 4.5. Dynamics of g_i changes depending on the *values* of steps (1), and the optimal trajectory of the control parameter (2) for the linear dependency of the step rates on the control parameter u .

4.4. NON-EMPIRICAL IDENTIFICATION OF THE MOLECULAR STRUCTURE FOR EFFECTIVE REACTION STIMULATORS AND INHIBITORS

To establish links between the structure of reacting particles and their reactivity is a fundamental issue of theoretical chemistry [30-36]. More often the issues on reactivity of atoms and molecules are discussed in connection with elementary reactions. Here, the rate constant and/or reaction cross-section serve as a measure of reactivity. Simultaneously, researchers focus their attention on developing strict principles that enable predicting the influence of the electron structure of reactants on the characteristics of a complex (multistep) chemical transformation.

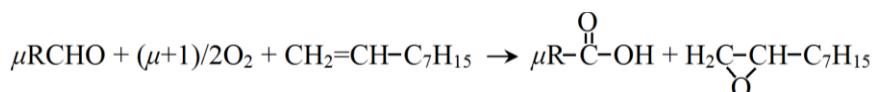
It should be noted that in case of multistep chemical reactions the problem of determining the reactivity of reagents is quite complicated, as the data (correct or intuitive) on species reactivity revealed from their participation in separate steps are “veiled” by the concentration dynamics of a complex chemical conversion. In other words, interrelated change in the concentrations of species creates serious barriers when trying to go deeply into the chemical essence of the reaction mechanism.

When discussing the factor related to the concentration evolution of a reaction system (Figure 4.6) one should make an essential stipulation. Separating the block of species concentration dynamics from that of information about the reactivity of species in elementary chemical reactions is some kind of abstraction. It is based on the independence principle between the specific rates of elementary reactions. Sometimes this principle may be violated because of the following reasons:

- a) violation of the Maxwell-Boltzmann distribution for the energy of particles,
- b) change in the properties of the reaction medium caused by occurring reactions.

Meanwhile, such problems may be overcome by a more detailed presentation of physical processes and changes of the reaction medium in kinetic models of complex chemical reactions. One can meet such a problem statement in [37].

Let us discuss qualitatively the questions arising at the solution of reactivity problems by the example of co-oxidation of *l*-nonene and an aldehyde [38]. With that end in view let us write down the gross-equation for this reaction:



where μ is the stoichiometric factor.

This reaction is of the chain nature yielding *l*-nonene oxide and appropriately carboxylic acid. From the practical viewpoint it is important to achieve the maximum useful regime for aldehyde utilization in the process of olefin formation. Usually this comes to the condition



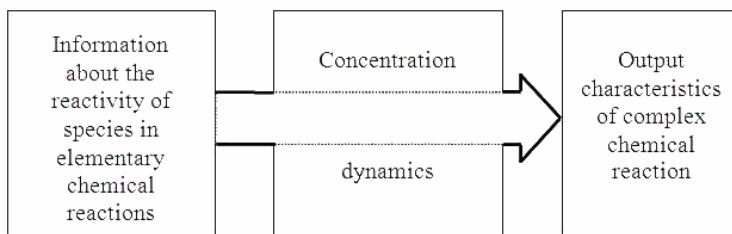


Figure 4.6. Formalized diagram for the influence of reactivity indices of species on the features of a complex chemical reaction.

This condition is satisfied by selecting a suitable aldehyde. However, because of the complicated chain nature of the reaction such a selection is not apparent. In the case under study, it is difficult to predict the structure of the substituent R in the aldehyde's molecule.

To understand the characteristic properties of the reactivity problem in multistep reactions let us highlight two important features, without pretending to give a strict description:

1. The reactivity of species in a multistep reaction is dependent on what target characteristic is chosen as its measure, namely: rate, selectivity, yield of reaction products, intensity of other features (luminescence, self-oscillations, criticality, etc.).
2. It is appropriate to perform a comparative analysis of the reactivity under the same conditions of the multisteps reaction: at the same temperature, concentration of initial reagents, state of a solid surface contacting with the reaction medium, etc.

The *value* analysis of the kinetic models, and as a consequence, the ranking of individual chemical transformations by their contribution into the resultant indicator of a chemical multisteps reaction, provides a basis which enables to retrieve information on the reactivity of the reacting particles. For example, it is possible to identify what chemical reactions involving an initial reagent and its intermediates play an important role and then to forecast how the change in the molecular structure of a reaction species will influence on the result of a complex chemical process.

Naturally, the readers remember that the *value* characteristics of steps are determined in the cases of small (local) perturbations in the initial rates of these steps. Consequently, inferences on the reactivity of a species in a complex reaction, based on the available contributions of individual steps and species should be made with some precautions, at least for the small range of change in the molecular structure of a reagent in the reaction system.

Nevertheless, in spite of the mentioned difficulties, the *value* interpretation of the reactivity enables to solve, strictly within a given kinetic model, the problem of the definition of the molecular structure for the reagent, leading to the target result of a complex chemical transformation [27,39-41].

Non-empiric identification of molecular structure for efficient reaction stimulators (initiator, catalyst, promoter) and inhibitors among a number of similar compounds, within the framework of the *value* approach, represents the clarification for a definite cluster of issues. In general, it is similar to finding the regime of optimal control, described in Section 4.3.1. We remind that the principle of Pontrygin's maximum is the theoretical basis for such

an approach. *For this latter case, the fact that the reactivity characteristics of the molecular structure of species act as the control parameters of a chemical reaction system is of fundamental importance.*

Finding the molecular structure for the efficient stimulator and inhibitor is carried out in the following way:

1. The first step is a selection of the target functional for a complex chemical reaction, which specifies the selected indicator's reactivity

$$I(t) = \int_0^t F(t) dt \rightarrow \text{extremum.}$$

2. Then the rate constants of steps with the participation of the reaction species under consideration and its intermediates are presented as functions of reactivity indices of the molecular structure in the initial form

$$k_i = \varphi_i(\mathbf{D}), \quad (4.33)$$

where \mathbf{D} is the vector of parameters specifying the reactivity. The dissociation energy of chemical bonds, the ionization potential, the electron density of reaction centers, the steric parameters and the other characteristics of the molecular structure, as a rule used by chemists to describe the reactivity of molecules and their fragments may serve as \mathbf{D} values.

The selection of either reaction indicies is mainly dictated by the necessity of their being described by means of dependences for reaction rate constants, together with both the participating species and the intermediate products of its conversion. Just in such a case, the *reactiivity characteristics of the initial reagent and its intermediates are system-matched*. For example, when modeling the inhibited liquid-phase oxidation of organic substances, the rate constants of reactions with the participation of the inhibitor (phenol) and the corresponding phenoxyl radical, may be expressed through the dependence on the dissociation energy of the hydroxyl OH-bond in the phenol molecule, the reactivity of which is considered (see [34] and Chapter 7).

In many cases $\log k_i$ is successfully presented in the form of a linear dependence on the parameters of electron structure \mathbf{D} , with satisfactory accuracy (see, for example, [30-36])

$$\log k_i = a_0^i + a_1^i D_1 + \dots + a_p^i D_p. \quad (4.34)$$

3. The corresponding kinetic equations and the Hamiltonian, in which the control parameters \mathbf{D} , are marked out, take the form

$$\frac{dc_i}{dt} = f_i(\mathbf{c}, \mathbf{k}, \mathbf{D}), \quad i = 1, 2, \dots, m \quad (4.35)$$

$$H = \psi_0 F + \sum_{i=1}^m \psi_i f_i(\mathbf{c}, \mathbf{k}, \mathbf{D}), \quad \psi_0 = \pm 1.$$

$\mathbf{D}(t)$ is assumed to be changing within the interval

$$\mathbf{D}(t) \in \mathbf{D}. \quad (4.36)$$

4. Then the procedure of finding the optimal control is carried out as described in Section 4.3.1. In accordance with the maximum principle the equation

$$\sup_{\mathbf{D}} H(\mathbf{c}, \psi, \mathbf{D}) = 0 \quad (4.37)$$

fits the condition (4.27). As described in Section 4.3.1 the solution of the system of differential equations (4.28) and at the same time the maximum condition (4.37) correspond to the optimal magnitude \mathbf{D}^* for which condition (4.27) is satisfied. The maximum principle also states the necessity to select \mathbf{D}^* from the boundary values $\mathbf{D}(t)$ and \mathbf{D}^{cl} , where \mathbf{D}^{cl} is defined by the condition

$$\frac{\partial H}{\partial D_i} = 0, \quad i = 1, 2, \dots, m.$$

The trivial condition on the invariance of parameters of molecular structure: $\mathbf{D}^* = \text{const}$ during the reaction simplifies the problem substantially. For the initial time the \mathbf{D}^* value fits to the parameters of molecular structure for the reaction stimulator and inhibitor that are effective for the given conditions. By this reason using equalities $\mathbf{D} = \text{const}$ and $H(t) = \text{const}$, the \mathbf{D}^* value may be computed already for the initial time.

5. The final stage of calculations is “decoding” the molecular structure for the efficient stimulator or inhibitor using the calculated \mathbf{D}^* value.

Very useful information is provided by the calculated kinetic trajectories of the *value* contributions of individual steps, for the cases when a stimulator or inhibitor with optimum molecular structure participates in a reaction. Ranking the steps by the contribution of reactions with participation of stimulators, inhibitors and their intermediates, enables to answer the question what reaction or reactions namely play the dominant role, and finally to determine the structure of the most efficient stimulator or inhibitor.

A specific illustration on the determination of the structure of an efficient inhibitor will be illustrated in Chapter 7 by the example of the model on chain oxidation of hydrocarbons (ethylbenzene) inhibited by phenols.

The above described procedure on finding the structure for the efficient stimulators and inhibitors obviously is based on the kinetic model. Here, the specification of equations (4.33) is also implied, which expresses the dependence of the rate constants of steps (involving the initial species of the reaction system and its intermediates) on the reactivity indices of the initial stimulators and inhibitors. However, in many cases just designing such kinetic models requires the serious creative efforts of researchers.

4.5. THE *VALUE* APPROACH IN EMPIRICAL CONTROL OF COMPLEX CHEMICAL REACTIONS

So far, when stating the *value* approach for the control of chemical reactions it was assumed that a researcher has enough information on the detailed mechanism of chemical transformation. Meanwhile, often the data on the reaction mechanism are incomplete, including those for commercially implemented processes. In such cases one has to rely upon *empirical methods*. As applied to complex chemical reactions, the empirical approaches are the subject of special discussion (see for example [42]). Here, on the basis of the available data, only some ideas about the basic principles of empirical modeling are presented.

The structure of realization of the empirical controlling is the same as for the nonempirical one. A crucial step is designing the reaction model followed by the evaluation of parameters.

Usually, the mathematical description of a dynamic model is given as follows

$$\frac{d\eta}{dt} = f(\mathbf{x}, \mathbf{u}) \quad (4.38)$$

where $\mathbf{u} = (u_1, \dots, u_m)$, $\mathbf{x} = (x_1, \dots, x_k)$ are the vectors of m control and k state variables, respectively, $\eta = (\eta_1, \dots, \eta_l)$ is the vector of l output parameters (concentrations, temperature, pressure, etc.).

For the empirical model the mathematical equations are often compiled proceeding from easy-to-use computation. Thus, the linear model is given by

$$\eta = x_0 + \sum_{i=1}^m u_i x_i . \quad (4.39)$$

If the linear model describes the character of a complicated process with poor accuracy, then polynomials of higher order are involved, or the output parameters are synthesized by the functions $\Phi_i(\mathbf{u})$

$$\eta = x_0 + \sum_{i=1}^m \Phi_i(\mathbf{u}) x_i , \quad (4.40)$$

where $\Phi_i(\mathbf{u})$ are selected on the basis of physicochemical considerations [43-45].

Assessment of the parameters of equations is a particular task of empirical modeling. Parameters of an empirical model are evaluated by methods of mathematical statistics, using the experimental data on kinetic curves that accumulate reaction species, the dependences of concentrations and their change rates on those of other reaction species, the initial conditions, etc. Description of methods of mathematical statistics, which assist in the determination of parameters for a reaction model may be found in [42-45].

The empiric approach appeared to be quite productive, enabling to solve a series of problems on controlling and planning the experiments for chemical systems, with insufficient information about their detailed mechanism. Nevertheless, when trying to estimate the real capabilities of empirical approaches, their cognitive importance appears to be not too high. Below, the specific features of empiric approaches are given, which according to M.Frenklach [42], restrict considerably the scope of their application.

1. The predictability of empirical models is insufficient, as they describe the process reliably, only within the limited range of conditions studied experimentally. At the same time this confines the acting interval of the selected control parameter.
2. Empirical models, as a whole, do not reveal the nature of chemical transformation.

It should be noted that in fact, the situation is not as desperate, as it seems at first sight. The capabilities and consequently the applicability of the empirical approaches are improved considerably, if the chemical reaction system is subjected to the preliminary *analysis of causes*. Here, under *analysis of causes*, it is meant representing the reaction system in any form, which reflects the cause-and-effect relation of conversion among the reaction species.

It is evident that the detailed reaction mechanism provides the most reliable information on the causal relationship. Nevertheless, the established sequence of conversion of the reaction species enables to use more effectively the incomplete, possibly the intuitive information on the complex chemical process.

We suppose that causal ordering of the reaction system, in spite of its conditional nature, expands substantially the predictability of the kinetic model as compared with the purely empiric approach. Obviously, the forecasting capabilities are strongly dependent on the fact, to what extent the kinetic model of a chemical reaction is based on real causes.

Note one more positive feature of the preliminary causal ordering of chemical reaction systems, is the enabling to group the parameters of a kinetic model to a great degree of reliability into the controlling and non-controlling ones, as well as to reduce their total number, which is very essential. This latter in turn enables to subject the parameters of a kinetic model and its output data to a thorough statistical analysis. The readers interested in a detailed analysis of the causes of complicated systems are referred to the monographs [46-48].

One of the most suitable forms for mapping the causation for chemical reaction systems are the so-called *flow graphs*. In this case the flow graph displays a sequence of conversions, representing a combination of interconnected steps, as the “precursor-product”. We suppose that the reader has a minimum knowledge on the graph theory, the main principles of which may be found in the books [49-55].

Below, the stages on composing the flow graph of a complicated chemical process are presented.

1. Selection of the reaction system species, which form the graph vertex consists of the conditional mappings of its constituent elements, as one of important stages of graph compiling. In this case, one can select the molecular species of the chemical process. Naturally, it is only one of the methods for the representation of the graph. The possibility is not excluded to select also the active intermediates [50], as well as the control parameters. At that, apparently it is necessary to rely upon the available information about the chemical process and the capabilities of the regression analysis to calculate the kinetic parameters of the empiric model.
2. The direction of causality, which in the chemical process is identical to a direction of transformation of one species into the other, is denoted by the arrows in the flow graph. As shown in Figures 4.7 and 4.8, nonlinear steps are marked by dotted arrows next to the main ones.
3. Kinetic equations for the selected reaction species are compiled by means of a flow graph. The change in reaction rate for the species is represented as a sum of rates for the paired transformations, taking into account the direction of arrows between the elements of the flow graph. Components of the rate, by some analogy with the law of acting mass, are proportionate to the concentration of the reaction species, from which the arrows of the flow graph are started. Then, the kinetic parameters of the flow graph are derived, as it was noted earlier, by means of the regression analysis, based on the kinetic equations and the available experimental data. It is assumed that these parameters are not time-dependent. They are independent, i.e. they have a meaning of effective rate constants for the paired interconvertible reaction species. When performing the regression analysis, it is also recommended to fix the values of those structural kinetic parameters of the graph that are reliably known *a priori*. In other words the quantitative data about a chemical transformation are used more completely.

The aforesaid suggests that a flow graph inherently enables the systematization of intuitive, qualitative and incompletely quantitative knowledge of a researcher and switch over the equation language. Let us illustrate this by the example of liquid-phase oxidation of benzaldehyde by dioxygen, which will be considered in more detail in Chapter 6 [29,56]. Let us suppose that the researcher possesses the following preliminary information about this reaction: (i) the peroxyacid is an intermediate product that results in benzoic acid directly or by interaction with the initial aldehyde; (ii) the oxidation is autoinitiated by the peroxyacid.

Let us compose the flow graph on the basis of mentioned information. Let us select the reaction molecular species: benzaldehyde, peroxybenzoic acid and benzoic acid as elements of the graph.

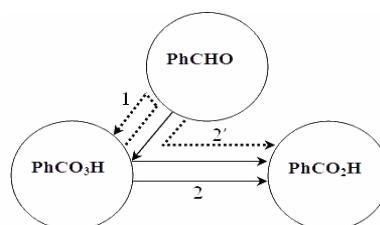


Figure 4.7. Flow graph illustrating liquid-phase oxidation of benzaldehyde by dioxygen.

Let us compile the corresponding equations for the variation rates of the selected reaction species:

$$\begin{aligned}
 -\frac{d[\text{PhCHO}]}{dt} &= (a_1 + a'_2)[\text{PhCHO}][\text{PhCO}_3\text{H}], \\
 \frac{d[\text{PhCO}_3\text{H}]}{dt} &= a_1[\text{PhCHO}][\text{PhCO}_3\text{H}] - \\
 &\quad -(a_2 + a'_1)[\text{PhCHO}][\text{PhCO}_3\text{H}], \\
 \frac{d[\text{PhCO}_2\text{H}]}{dt} &= (a_2 + a'_1)[\text{PhCHO}][\text{PhCO}_3\text{H}],
 \end{aligned} \tag{4.41}$$

where a_i are the kinetic parameters of the flow graph ($i = 1, 2, 2'$), having a meaning of the effective rate constants of reaction steps.

For comparison the similar equations for the same reaction species are deduced, derived from the detailed reaction mechanism in an approximation of the stationarity by free radicals (see Chapter 6)

$$\begin{aligned}
 -\frac{d[\text{PhCHO}]}{dt} &= \left(\frac{k_3 k_4}{k_6} + k_5 \right) [\text{PhCHO}][\text{PhCO}_3\text{H}], \\
 \frac{d[\text{PhCO}_3\text{H}]}{dt} &= \frac{k_3 k_4}{k_6} [\text{PhCHO}][\text{PhCO}_3\text{H}] - \\
 &\quad -(k_4 + k_5 [\text{PhCHO}])[\text{PhCO}_3\text{H}], \\
 \frac{d[\text{PhCO}_2\text{H}]}{dt} &= (k_4 + k_5 [\text{PhCHO}])[\text{PhCO}_3\text{H}].
 \end{aligned} \tag{4.42}$$

Comparing equations (4.41) and (4.42) it is easy to observe their identity. It is an evidence of the good capabilities of the empirical approach, based on the preliminary causal structuring of the chemical reaction system. But here, as it seems to us, an important reservation should be made. Significant discrepancies might be observed with the non-empirical methods in more complicated cases and when there is less information on chemical transformation.

To have a more complete view about the opportunities of the method under consideration, let us give one more example. Let us plot the flow graph and the corresponding kinetic equations for the liquid-phase oxidation of ethylbenzene, (PhCH_2CH_3) by dioxygen [2, 56, 57]. Similar to the example discussed above, let us provide the preliminary information about this reaction:

- Hydroperoxide of ethylbenzene ($\text{Ph}(\text{CH}_3)\text{CHOOH}$), methylphenylcarbinol ($\text{Ph}(\text{CH}_3)\text{CHOH}$) and acetophenone ($\text{Ph}(\text{CH}_3)\text{CO}$) are the major products of the reaction.
- The reaction is autoinitiated by hydroperoxide.

- c) Methylphenylcarbinol and acetophenone are formed both from the hydroperoxide and by the autoinitiated conversion of the initial ethylbenzene omitting the hydroperoxide.
- d) There also are ways for the conversion of methylphenylcarbinol and hydroperoxide into acetophenone under the autoinitiated mode.

The information cited is enough for plotting the flow graph for the reaction under consideration (Figure 4.8). This graph enables the compiling of the corresponding kinetic equations for reaction species

$$\begin{aligned}
 -\frac{d[\text{PhCH}_2\text{CH}_3]}{dt} &= (a_1 + a_2 + a_3)[\text{PhCH}_2\text{CH}_3][\text{Ph}(\text{CH}_3)\text{CHO}_2\text{H}] \\
 \frac{d[\text{Ph}(\text{CH}_3)\text{CHOOH}]}{dt} &= a_1[\text{PhCH}_2\text{CH}_3][\text{Ph}(\text{CH}_3)\text{CHOOH}] - \\
 &\quad -\{(a_2 + a_3)[\text{PhCH}_2\text{CH}_3] + a_4 + a'_5 + a_5[\text{Ph}(\text{CH}_3)\text{CHOH}]\}[\text{Ph}(\text{CH}_3)\text{CHOOH}], \\
 \frac{d[\text{Ph}(\text{CH}_3)\text{CHOH}]}{dt} &= \{a_3[\text{PhCH}_2\text{CH}_3] + a_4 - a_5[\text{Ph}(\text{CH}_3)\text{CHOH}]\}[\text{Ph}(\text{CH}_3)\text{CHOOH}]
 \end{aligned} \tag{4.43}$$

In order to avoid overtiring the reader we will skip the kinetic equations that are derived from the detailed reaction mechanism of the liquid-phase oxidation of ethylbenzene. This is if, for example, referring to [2,57] one can make certain of the equivalence between the equations derived by the empirical and non-empirical ways. Similar equations might be obtained if one supposed from the outset that the quadratic termination of the chain carriers is peculiar to the reaction considered. Consequently, this would result in a square root dependence for the accumulation rates of reaction species on the concentration of hydroperoxide, which is responsible for the autoinitiation of reactions.

For all, it would be emphasized once again that thoughts about the existence of ready formulas at composing flow graphs seems to be too optimistic. Evidently, here much is dependant on the volume of the available information about the chemical reaction, its reliability level, somewhat from the researcher's intuition, and naturally from the goals set.

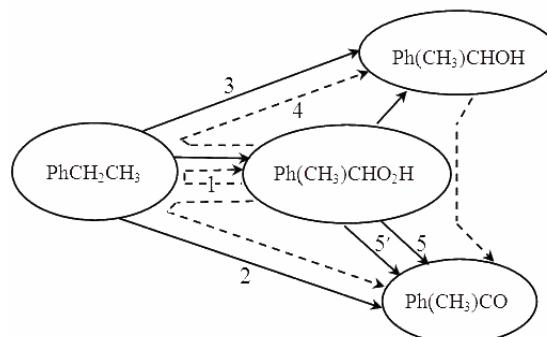


Figure 4.8. Flow graph illustrating liquid-phase oxidation of ethylbenzene by dioxygen.

Now let us proceed to the discussion of opportunities of the *value* approach in the empirical control of complex reactions [27]. Here, application of the given method results in practically the same benefits as in the case of the non-empirical approach. Applying this approach in the empirical control of chemical processes comes to solving the following problems:

- Ranking the reaction steps and species by their *value* contribution in the empirical reaction model. In this case the mathematical formalism described in section 4.3.1 remains unchanged.
- *Value* ranking the steps and species enabling the most operative control parameters to be selected “chemically” more intelligently and far successfully, rather than from a “pure” empirical approach.
- Determination of the controlling regime leading to the reaction’s optimum result.

Let us turn again to the example of relatively simple reaction of benzaldehyde oxidation, to carry out a brief and to some extent qualitative discussion on the opportunities of the *value* approach in empirical controlling. Our end goal is to achieve the maximum selectivity for the yield of peroxybenzoic acid. Let us suppose the carried out regression analysis is strictly enough. Then, the quantities a_i will approximate to those of proper parameters, combinations of rate constants as obtained by the detailed analysis of the reaction mechanism. At that a_i values are determined by comparing equations (4.41) and (4.42), according to the numerical values of the rate constants of the reactions presented in Table 6.1 (see Chapter 6). Numerical calculations using equations (4.41) and (4.42) in the framework of the canonical equations (4.28) make it possible to single out link 1 as the dominant, for which a positive *value*, $G_1^{\text{PhCO}_3\text{H}} > 0$ is registered during the entire reaction. In this case, Pontryagin’s principle of maximum recommends the maximum strengthening of this link. Further reasoning is constructed as follows. As the link 1 is strengthened by degenerate branching, so the most evident way to increase the selectivity is increasing the rate of free radical initiation from the peroxyacid. This is achieved either by the selection of a catalyst that has maximum activity with respect to the peroxyacid’s decomposition, yielding free radicals or increasing the catalyst’s concentration.

Thus, the empirical method described in this section coupled with the *value* approach permits in principle, even if there is only qualitative information about the reaction, to obtain the same result as the non-empirical approach does in the presence of complete information (see Chapter 6).

4.6. Considerations Related to Features of *Value* Quantities

Numerical methods in chemical kinetics are used traditionally to calculate the kinetic trajectories of concentrations of the species of complex (multistep) chemical reactions, on the basis of their mathematical models. In particular, such models are then corrected after comparisons are made between the experimental data and computational results.

Accordingly, special numerical methods for the analysis of reaction mechanisms are applied. These reveal the individual excessive steps, aim to reduce the initial kinetic models

and specify the most important steps for the purpose of finding the most effective way to describe the influence of complex chemical reactions. Generally, these are reduced to calculating the kinetic significance of the chemical species and the individual steps in the reaction kinetic model, according to previously specified relevant criteria.

In these cases, the method of parametric sensitivity analysis has received the broadest acceptance. In this method, often the calculation of time profiles of the derivatives of species concentrations is made by the values of rate constants in individual steps as the initial computing procedure [58,59]. Also, methods are applied to analysis the rates of individual steps and to separate the contributions of individual steps in the total change of the Gibbs free energy or entropy that enter into the overall chemical transformations [60].

Our suggested method of numerical *value* analysis for the mechanisms of complex reactions is based on the use of the system of Hamiltonian equations for the mathematical modeling of reactions, with separation of the targeted functional that characterizes the quality of the selected chemical reaction.

Essentially, the Hamiltonian controlling mechanism is founded on the basis of the *value* method. When using this approach by understanding the physical-chemical and kinetic properties, unavoidably this results into two new conjugate variables to describe the kinetic system, whereby the *value* of chemical species and the individual steps are specified, which characterize the kinetic system's significance via the target functional of the selected reaction.

The above-mentioned commonly used method of sensitivity analysis with respect to the rate constants of individual steps is aimed at identifying the rate-limiting individual steps of the mechanism of a complex chemical transformation. Meanwhile, *value* magnitudes are allocated according to the target characteristics of a reaction that clearly describe the role of the chemical species and the individual steps, in terms of controlling complex reactions.

For this reason, *value* analyses can substantially supplement the numerical information on the significance of chemical species and individual steps obtained by other methods, thus enabling to more definitely and rigorously identify the effective levers of controlling chemical reactions. It is also important that the *value* analysis of the mechanisms of complex reactions be characterized by simplicity and clarity of calculational procedures to obtain readily the numerical data.

When we compare our *value*-based approach with other methods of sensitivity analysis, the following important features of the *value* method are distinguishing:

- It reveals numerically the kinetic significance of the chemical species and the individual steps, taking into account their contribution in the specified target functional of a complex chemical process;
- It overcomes the problem of “zero” parametric sensitivity, when very small values of the parametric sensitivity of steps do not allow to consider them as superfluous steps of the reaction kinetic model;
- It reveals more rigorously the effective characteristics of the chemically meaningful control of reactions;
- It determines numerically and interprets chemically the reaction critical conditions on the basis of the kinetic model. This issue will be discussed in next chapters.
- It identifies the molecular design of the efficient (optimal) promoters and inhibitors of reactions among a number of similar compounds.

4.7. ARGUMENTS ON THE OBJECTIVITY OF THE VALUE IDEAS IN CHEMICAL KINETICS

In this Section we intentionally pass over the discussion concerning the objectivity of concepts that disclose the core of phenomena. This is a matter of special description (see, e.g. [61,62]). Nevertheless, let us bring the definition that seems to be more attractive concerning the “objectivity” of variables of a dynamic system. Target variables imply a minimum set of used characteristics with maximum universality, hence for a maximum range of mapping the system behavior.

At the same time, concerning the “objectivity” concept of characteristic quantities, it seems very useful to follow the analog method. Essence of the latter comes to the acceptance of general principles that withstood tests by numerous experimental observations in the various fields of science. Description of dynamic systems [63,64] is a successful example in this context. It is reasonable to suppose that the different forms of motion of matter including chemical transformation have to be characterized by analogous concepts from the most general standpoint. Let us try to offer arguments in favor of this statement. Thus, when describing the behavior of dynamic systems the extremality problem must be solved. For the solution of such problems in the traditional interpretation, a conflict among two variables conjugated to each other is inevitable. Of the two the former describes the quantitative and the latter the “qualitative” (*value*) side of the dynamic system’s behavior. Namely, through the mutual links of quantitative and qualitative variations in the dynamic system, the laws of motion are revealed.

Certainly, when solving the problems of targeted influence on a complex reaction we deal with the extremality task. A similar situation arises when the problem is set to describe the behavior of a chemical reaction system, namely, in the identification of the kinetic model, which describes experimental results to the best advantage and possesses a maximum of prognostic capability. To attain this end the following approaches highlighted in the above are usually used:

- specification of quantitative characteristics of the kinetic model;
- supplementing the kinetic model by new steps;
- reducing the redundant models of reaction systems;
- planning and performing experiments to update the kinetic model.

It may be concluded from the aforesaid that proceeding from the extremality task, apart from the quantitative characteristics, one has to act with the qualitative (*value*) ones of the reaction system.

It is interesting to draw some analogy between a complex chemical reaction and a dynamic system, which consists of material points. The theoretical mechanics describes the state of such a system by means of the classical (canonical) equations of motion [63,64] based on a vast theoretical and experimental foundation

$$\begin{cases} \frac{dx_i}{dt} = \frac{\partial H}{\partial p_i} = f_i \\ \frac{dp_i}{dt} = -\frac{\partial H}{\partial x_i} = -\frac{\partial U}{\partial x_i}, \quad i = 1, 2, \dots, m, \end{cases} \quad (4.44)$$

where m is the number of material points in the Hamiltonian system

$$H = -(T - U) + \sum_i p_i f_i,$$

and where T and U are the kinetic and potential energies of the system, respectively; f_i , p_i , x_i are the velocity, momentum and coordinate of the i -th material point, respectively.

Simultaneously, according to a fundamental principle of theoretical mechanics, *the principle of least action*, the motion of the system of material points obeys the key condition:

$$\int_0^t (T - U) dt \rightarrow \min. \quad (4.45)$$

It follows from equations (4.44) that the dynamic behavior of a system is simultaneously determined by the equations of motion of both the velocity of material points and the velocity of momentum variations. The variation of momenta with time informs about the “relief” of the target parameter (in this case the energy) that determines the system’s motion. Note that according to our definitions, momentum is nothing else than the “value” of a material point in target quantity - the difference of the kinetic and potential energies

$$p_i = \frac{\partial(T - U)}{\partial f_i}. \quad (4.46)$$

Thus, a dynamic system is objectively mapped in the phase space of m coordinates and proper m momenta: $\{x_i, p_i\}$.

Developing such a reasoning, a chemical reaction may be considered as the result of motion of concentration points. It follows from this idea that just like the system of material points, a complete description of the evolution of a complex chemical reaction, besides the kinetic equation requires data on the “relief” of the reaction’s target characteristic. For this, similar to theoretical mechanics, it is necessary to determine the *values* of motion velocities of concentration points as it is made for the momenta. The latter, as we made certain, are easily transformed to *values* of the reaction steps. The arguments cited are well-grounded both for controllable and uncontrollable chemical processes. In other words, the objectivity of *value* parameters in the description of complex reaction kinetics is warranted, whether extreme conditions for the target functional of chemical process are kept or not.

Summarizing, it should be noted that the *value* approach inherently relies on the classical-canonical description of kinetic laws of multistep chemical reaction systems. As a result, a multistep chemical transformation is more completely described by the phase space of the

concentration of species and their *values* $\{c_i, \psi_i\}$ or accordingly, by the phase space of the rates and *values* of reaction steps $\{r_j, G_j\}$.

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Chapter 5

KINETICS OF MULTICENTERED CHAIN CHEMICAL REACTIONS. *VALUE* APPROACH

This chapter provides a formal kinetic description of multicenter chain reactions, where in the rate-limiting steps several carrier chains participate simultaneously. Internal system relations in a multicenter chain reaction are discriminated by the chain length. components These quantities are considered as a response of the rate of formation of some reaction product, due to a small change in the rate of origination of certain chain carrier. The issues of organic connection of *value* quantities with characteristic quantities of multicenter chain reactions are discussed.

Within the frame of the *value* approach a new numerical method is proposed for the identification and study of critical phenomena in branched chain reactions, according to their kinetic models. As a criterion for the critical states of a reaction system its state of extreme behavior is proposed. This allows to consider the initial conditions and parameters of the reaction system as controlling parameters, on the base of which the critical states of reactions are searched. Calculations are performed using the Maximum Principle with simultaneous revealing the *value* characteristics for individual steps and chemical species. With the help of *value* quantities the “chemical content” of critical states for nonbranching chain reactions are numerically illuminated.

In this chapter we will pay attention to the application of the *value* approach to chain chemical reactions, guided mainly by the following reasons:

First, chain chemical reactions belong to the class of reactions for which the general kinetic laws are studied in detail and the theoretical fundamentals are formulated on the whole. It is thought that the possibilities of the theoretical prerequisites of the *value* method will be more clearly highlighted against this background.

Second, namely with the chain reactions is connected the discovery of one of the most interesting properties of chemical reactions, which are the critical phenomena [1-5]. The universality of theoretical tools to analyze kinetic models is verified also by their ability to reveal and study the critical states of reaction systems.

And third, chain chemical reactions are at the basis of many modern technologies [6-8], and the problem of efficient control of these processes is crucial.

This Chapter is planned in the following logical sequence. In the beginning, a formal-kinetic description of multicentered chain reactions [9] is presented. Then, arguments are listed relative to what additional information may be retrieved by applying the *value* approach, as already stated in the preceding Chapters. Finally, in summary the *value* approach

for the identification and studying of critical phenomena in branching chain reactions is described, based on their kinetic models.

5.1. Formal Kinetics of Multicentered Non-Branching Chain Reactions

Frequently, the basic kinetic laws of chain reactions are described in the one-centered approximation [1]. Certainly such an “ideal” situation is not of general nature. It is easy to note that even a relatively simple example of a chain chemical reaction between molecular hydrogen and chlorine is realized by means of two active reaction centers, the chain carriers, the H and Cl atoms.

Multicentered consideration of a chain reaction, unlike the one-centered one, takes into account from the outset the possibility of the decisive role of a great number of individual steps involving the different active reaction centers. Moreover, very often such important reaction features as the reactivity of initial reagents, the yield of target products, etc. are determined by the intensity of the chain reaction occurring by means of different “paths”. It is easy to conceive that the one-centered approach is not appropriate when studying such problems.

Let us pass to a brief description of the formal kinetics of multicentered chain reactions. A multicentered non-branching chain reaction with linear steps of transformation of the active reactive centers (chain carriers) may be represented in the form of a formal scheme [9], as some kind of a flow graph for the dynamic process (see Section 4.5).

The fact that in a multicentered approach the chain process is described by species chains generated by different active centers is the distinguishing feature, as compared to the one-centered approach. This statement needs to be explained further. Thus, the product P_i is formed by the chains initiated by different active centers R_j . The key parameter discriminating the chain ways, which result in the formation of the product P_i is a *chain length component* v_j^i .

In the presented model scheme for a chain chemical process with linear steps of transformation of active reaction centers, the initiation steps act independently. In this case the rate of the formation of the P_i product may be written as the sum of rates, corresponding to the different directions of the chain reaction

$$r_{P_i} = \sum_{l=1}^n r_l^0 v_l^i = r_R^0 v_{av}^i, \quad (5.1)$$

where $r_R^0 = \sum_{l=1}^n r_l^0$ is the overall rate for the chain carrier initiation; l is the number of an arbitrary active center by which the summation is performed; n is the number of active reaction centers of the chain process; and v_{av}^i is the average length of the chain yielding the i -th product, defined as

$$v_{av}^i = \frac{\sum_{l=1}^n r_l^0 v_l^i}{\sum_{l=1}^n r_l^0} . \quad (5.2)$$

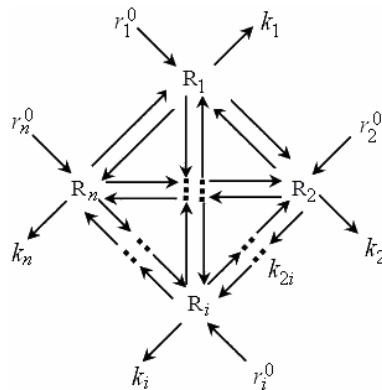


Figure 5.1. Schematic illustration of a multicentered non-branching chain reaction. R_i is an active reaction center (atom, free radical, excited particle, etc.). Arrows between active reaction centers, chain carriers, R_i and R_n , denote the reactions resulting in mutual transformations; k_{ij} is the effective rate constant for the formation of the R_j reaction center with participation of the R_i reaction center; k_i is the reaction rate for the termination of the active reaction center R_i ; and r_i^0 is the rate of initiation of the active reaction center R_i .

Thus, equation (5.1) is a result of the system structurization of the fundamental relationship of chain reactions (Chapter 1, equation 1.8). At the same time from (5.1) we have

$$v_l^i = \frac{\partial r_{p_i}}{\partial r_l^0} . \quad (5.3)$$

The chain length components v_l^i specifies the value for the step of the active reaction center (R_l) initiation, resulting in the product P_i [9]. And the product $r_l^0 v_l^i$ has to be considered as the value contribution for the step of the active reaction center (R_l), yielding the product P_i .

Within the framework of the traditional interpretation of chain length, the chain length component v_l^i represents the mean number of chain links that result in the product P_i , introducing the active center R_l into the reaction system. It should be reminded that the chain link in turn represents a cyclic process, involving the successive stages of chain propagation, where the active species originating this sequence are reproduced again.

Obviously, under conditions of the multiroute nature of the chain process, the product P_i may appear in different chain links. Thus, for a chain reaction with three chain carriers, the corresponding links of the chain length component v_l^i for the P_i product formation, initiated by the active center R_i , are illustrated in Figure 5.2.

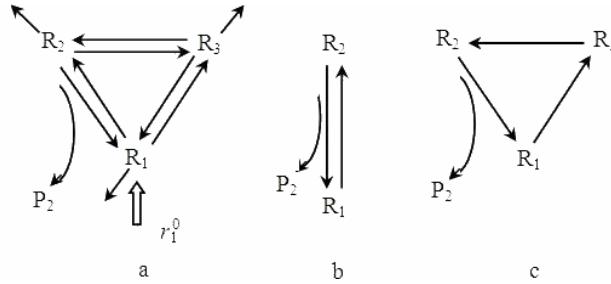


Figure 5.2. Links (b,c) of chain species, v_1^2 , of the P_2 product formation in the chain process (a) initiated by active reaction centers R_1 . The rate of P_2 product formation is $r_{P_2} = k_{21}[R_2]$.

Now let us derive the analytic dependence for the rate of the P_i product formation and the chain length component v_j^i , on the quantitative characteristics of individual steps (r_i^0, k_{li}, k_i), for the multicentered non-branching chain process [9]. In accordance with the reaction scheme illustrated in Figure 5.1 the rates of the chain carrier formation are:

$$\begin{aligned} \frac{d[R_1]}{dt} &= r_1^0 + k_{21}[R_2] + \dots + k_{n1}[R_n] - [R_1] \left\{ k_1 + \sum_{i=1, i \neq 1}^n k_{li} \right\}, \\ \frac{d[R_l]}{dt} &= r_l^0 + k_{l1}[R_1] + \dots + k_{nl}[R_n] - [R_l] \left\{ k_l + \sum_{i=1, i \neq l}^n k_{li} \right\}, \\ \frac{d[R_n]}{dt} &= r_n^0 + k_{1n}[R_1] + \dots + k_{n-1,n}[R_{n-1}] - [R_n] \left\{ k_n + \sum_{i=1, i \neq n}^{n-1} k_{ni} \right\}. \end{aligned} \quad (5.4)$$

For the steady-state condition in active reaction centers

$$d[R_i]/dt = 0, \quad i = 1, 2, \dots, n$$

the differential equations (5.4) are transformed into a system of algebraic equations. From this system $[R_i]$ values may be calculated as [10]

$$[R_i] = \frac{D_i}{D}. \quad (5.5)$$

on condition that $D \neq 0$.

$$D_i = (-1)^{i+1} r_1^0 |M_1^i| + \dots + (-1)^{i+n} r_n^0 |M_n^i|, \quad (5.6)$$

where $|M_j^i|$ is the minor of the determinant D_i , and D is the main determinant of the system of equations.

From equations (5.5) and (5.6) we have

$$r_{p_i} = k_{\text{eff}} [R_i] = k_{\text{eff}} \{ (-1)^{i+1} r_1^0 |M_1^i|_i + \dots + (-1)^{i+n} r_n^0 |M_n^i|_i \} / D, \quad (5.7)$$

where $k_{\text{eff}} = k_{p_i} [A]$ is the kinetic factor, k_{p_i} is the rate constant for the transformation of the initial substance A to the product P_i with the participation of the active reaction center R_i .

Equation (5.7) confirms the validity of expression (5.1) based on the representation of the rate of the P_i product formation, as a sum of the rates of chain conversions generated by the different chain carriers. Comparing (5.1) and (5.7) one obtains

$$v_j^i = \frac{k_{\text{eff}} (-1)^{i+j} |M_j^i|_i}{D}. \quad (5.8)$$

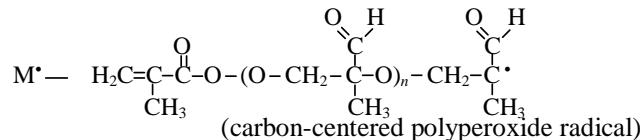
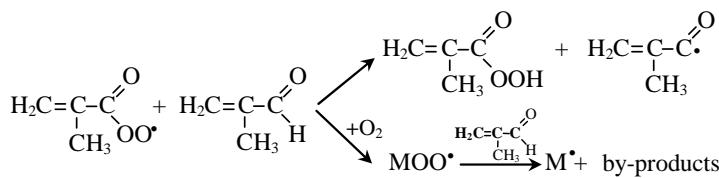
Thus, the chain length component is quite a meaningful quantity from the kinetic viewpoint, which is determined also by the alternative method based on a stochastic interpretation [11].

5.2. SELECTIVE INITIATION AND INHIBITION OF MULTICENTERED CHAIN REACTIONS

According to the one-centered consideration of the chain reactions (see Chapter 1), possibility of changing the selectivity in the formation of the reaction products by means of stimulating-generation or removal of certain reactive centers, is not foreseen. Moreover, independency in the behavior of the chain process on the type of such active centers introduced into the reaction system [1] was often thought to be a specific feature of the chain nature of a chemical transformation. In other words, the initiation was solely understood as a “trigger” of a chain reaction. Meanwhile, in accordance with theoretical concepts on the multicentered nature of chain conversions (equation 5.1), the initiation rates of active reaction particles in principle may differently affect the rate of reaction product formation, i.e. to have a different value and consequently contribution in r_{p_i} . As a result of such an approach, a conclusion was made on a basically new opportunity for changing the relative rates of the products formation, when changing the initiation or termination rates of the chain carriers [9]. This is carried out using initiators and inhibitors that result in increase in the selectivity of target product formation. For the first case as if the reaction pathways yielding target products are “independently” intensified, and in the second case when applying an inhibitor, solely undesirable direction of reaction is decelerated, that is selective inhibition of chain reaction is implemented.

The phenomenon of selective inhibition of chain reactions was for the first time explained by N.M. Emanuel, E.A. Blumberg, L.A. Tavadyan and S.A. Maslov [11]. It was experimentally observed in a number of liquid-phase oxidation reactions. Thus, introducing small amounts of an additive stable nitroxyl radical (4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl, TEMPOL) and a heterogeneous inhibitor (WSe₂) makes it possible to increase the selectivity of formation of unsaturated acids and epoxides in chain oxidation reactions of α -methylacrolein, 2-ethylhexenal, as well as co-oxidation of aldehydes and olefins (Table 5.1).

In particular, the formal scheme of chain conversions for oxidation of unsaturated aldehydes is presented as follows:



The principal condition for realization of the chain reaction selective inhibition is defined as a need in low intensity of the transformation reactions of polyperoxide radicals, MOO^\bullet , M^\bullet (which are responsible for by-products formation) into acylperoxyl ones, yielding target products.

The concept on multicentered reaction system of chain conversion [9] (Section 5.1) enables to consider the conditions of both the selective inhibition and selective initiation of chain reactions from the more general viewpoint.

Table 5.1. Selective inhibition of chain reactions on autoxidation of unsaturated aldehydes and co-oxidation of styrene and acetaldehyde (the conditions of reactions are described in [11-13])

Reaction mixture	In	K^* , %	Target products	S (mol %)	
				without In	with In
$\text{CH}_2=\overset{\text{O}}{\underset{\text{CH}_3}{\text{C}}}\text{H} + \text{O}_2$	RNO^\bullet	41	$\text{CH}_2=\overset{\text{O}}{\underset{\text{CH}_3}{\text{C}}}\text{OH}$	39	84
$\text{C}_3\text{H}_7\text{CH}_2=\overset{\text{O}}{\underset{\text{C}_2\text{H}_5}{\text{C}}}\text{H} + \text{O}_2$	RNO^\bullet	45	$\text{C}_3\text{H}_7\text{CH}_2=\overset{\text{O}}{\underset{\text{C}_2\text{H}_5}{\text{C}}}\text{OH}$	45	85
$\text{C}_3\text{H}_7\text{CH}_2=\overset{\text{O}}{\underset{\text{C}_2\text{H}_5}{\text{C}}}\text{H} + \text{O}_2$	WSe_2	45	$\text{C}_3\text{H}_7\text{CH}_2=\overset{\text{O}}{\underset{\text{C}_2\text{H}_5}{\text{C}}}\text{OH}$	45	72
$(\text{CH}_3\text{CHO} + \text{C}_6\text{H}_5\text{CH}=\text{CH}_2) + \text{O}_2$	RNO^\bullet	67	$\text{C}_6\text{H}_5\text{CHO}$ $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$ $\text{C}_6\text{H}_5\text{CH}-\text{CH}_2\text{O}$	47	91**

* S , K are reaction selectivity and conversion, respectively; In denotes inhibitor;

** Selectivity is calculated by the sum of three target products;

RNO^\bullet denotes stable radical TEMPOL: $\text{HO}-\text{C}_6\text{H}_3-\text{NO}$

Differential selectivity of a chemical reaction is defined as follows (see Chapter 4):

$$S_d = \frac{f_i r_{P_i}}{r}. \quad (5.9)$$

The following inequality meets the condition of selective initiation of chain reaction by free radicals of R_i type

$$\frac{\partial S_d}{\partial r_i^0} > 0. \quad (5.10)$$

In expression (5.10) the sign "greater" indicates that the possibility to increase the selectivity of target product formation is of practical interest.

As shown in [9] the condition of selective initiation of chain processes is transformed into the following inequality:

$$v_l^i > v_{av}^i. \quad (5.11)$$

Simultaneously it follows from the condition (5.11) that the chain length component initiated by the R_i chain carrier at the minimum exceeds one of those initiated by the arbitrary chain carrier

$$v_l^i > v_j^i. \quad (5.12)$$

It should be highlighted once again that the chain length component v_l^i , having the *value* meaning, is a key parameter specifying differentiation of links in the reaction system of chain conversion. So, the number of discriminating magnitudes of the chain length components as if defines the number of degrees of freedom for multicentered chain reaction. This number determines integrally the amount of possible alternatives for the change of relative rates of chain reaction directions, consequently the selectivity of the process, when the initiation rates of certain chain carriers are varied.

For the sake of obviousness let us illustrate the possibility of the P_2 product formation with participation of four types of chain carriers, as a result of selective initiation by the chain carrier R_1 . According to (5.12) one of the conditions for the realization of this possibility is the weak evolutional periodic link between the active reaction centers R_2 and R_3 and/or R_4 , which corresponds to the following formal scheme of conversions:

Selective initiation and selective inhibition of multicentered chain reaction as a whole are identical in nature. Expressions (5.11) and (5.12) may be also considered with certain reservations as conditions for the selective inhibition. More detailed formal-kinetic analysis of the possibility to realize selective inhibition in the framework of multicentered consideration of chain conversion may be found in [9].

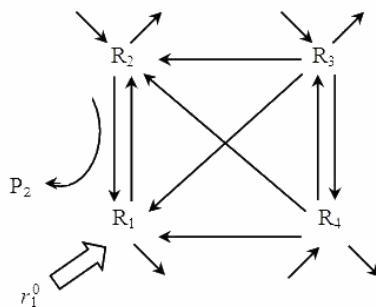


Figure 5.3. Schematic pattern of a non-branching chain reaction with participation of four types of chain carriers. r_1^0 is the rate of initiation of the R_1 chain carrier.

5.3. VALUE ANALYSIS OF KINETIC MODELS OF CHAIN REACTIONS

Formal kinetic interpretation of multicentered chain reactions applied in the preceding section was aimed at providing a methodology and to some extent knowledge. Obviously, a comprehensive use of the formal approach is justified for a limited number of the chemical reaction mechanisms. Among such ones are the kinetic models, which yield to the linear formalization. Challenges also arise connected with such limitation as the possibility to examine only the steady-state condition of the chain process without taking into account a time-dependent change in the reaction composition.

Now assuming as a basis the methodology of considering the chain reactions as reaction systems let us comment on the application capabilities of the *value* analysis method, on the basis of the Hamiltonian systematization of kinetic models [9,12-25].

Certainly here the problems and issues of general nature may be solved independent of the chain nature of the reaction. They are discussed in detail in Chapters 3 and 4. We remind these problems once more.

1. *Value* identification of the kinetic significance of the individual steps and chemical species of a chain reaction.
 2. Identification of the “base” - reduced reaction mechanism. An example on the identification of such a mechanism of the chain reaction is illustrated in Chapter 3.
 3. Broadening the possibilities on planning the experiments aimed at specifying the chain reaction mechanisms.
 4. Developing new approaches for goal-directed impact on a reaction. As an appropriate example may serve the prediction of the growth in the selectivity of a chain reaction by selectively inhibiting its undesirable pathways, as demonstrated in Chapters 5 and 6.
 5. Defining the structure of an effective reaction stimulator or inhibitor resulting in extreme cases, based on a specified kinetic reaction model. Such a method is illustrated by the example of non-empirical selection of the efficient inhibitor for the chain reaction of liquid-phase oxidation of ethylbenzene and methyl linoleate (see Chapter 7).
 6. *Value* control of chain reactions.

Nevertheless let us highlight two aspects specific for the chain reactions. Firstly, the *value* analysis method of kinetic models enables to reveal and examine the critical phenomena inherent to branching chain reactions. The results of such investigations are presented in the next paragraph. Secondly, the parametric corollaries (ψ_i) of the *value* method impart a new meaning to the introduced important feature of chain reactions, the chain length component v_i^j .

When using the target functional describing the concentration change of the reaction product c_j

$$I(t) = \Delta c_j(t) = \int_0^t f_j(t) dt, \quad (5.13)$$

then as shown in [11], the derived *value* quantities ψ_i for reaction centers i at reaction times commensurable to the chain development time take the meaning of the chain length component

$$v_i^j = \psi_i^j(t) = \frac{\partial f_j[f_1(t), \dots, f_m(t)]}{\partial f_i} \Big|_{f_i = f_i(t_0)}. \quad (5.14)$$

As a whole, the *value* quantities $\psi_i^j(t)$ especially for chain carriers provide data about the “structure” of reaction system. In this way one can conclude on the degree of chain reaction “centricity” based on the magnitudes ψ_i . For example, for the chain reaction of hydrogen with chlorine or liquid-phase oxidation of hydrocarbons described in Chapter 1, ψ_i is the same for all chain carriers. This is an evidence that the considered chain reactions are one-centered. We suppose that the degree of “centricity” of chain reaction is determined by the number of significantly different ψ_i magnitudes for chain carriers. Liquid-phase oxidation of α -methylacrolein considered in Chapter 6 is such an example.

Thus, figurative concept of the avalanche-like occurring of the chain reaction is very productive to describe the general laws of chain processes. However we suppose that focusing attention on the presence of inner “relief” of the avalanche itself is quite useful. We believe that *value* parameters enable to highlight this relief.

5.4. VALUE APPROACH FOR ANALYSIS OF CRITICAL PHENOMENA IN BRANCHING CHAIN REACTIONS

In Chapter 1 we briefly considered the critical phenomena in branching chain reactions consisting in the qualitative transfer from the slow mode of reaction to the intensive (self-accelerated) one at negligible changes in the parameters of a reaction system. Investigations of critical phenomena are still urgent. Increased interest in this problem is closely associated with the practical tasks of combustion, fire and explosion safety, inhibition of oxidation processes, etc. [1-3, 26-50].

The problem on determining the explosion limits was elegantly solved by N.N. Semenov within the framework of the one-centered approach (see Chapter 1), applying the method of partial stationarity by the concentrations of chain carriers. Meanwhile, often a challenge is faced when, for defining the critical conditions for the chain reaction, it is necessary to take into consideration some important factors, such as the multicentered nature of the reaction system, the non-isothermal conditions of the reaction, the nonstationarity of phenomena due to a change in concentration of initial and intermediate products, including the reaction chain carriers at attaining the critical state, the explosion limit. In such a case defining the critical states becomes an intractable problem [35-50] due to the complicated nonlinear dynamics laid down into the kinetic models of chain reactions.

We believe that the versatile nature of the *value* analysis method of multistep mechanisms may be highly beneficial in studying the nature of critical phenomena. We also were guided by the fact that up-to-date methods for describing critical phenomena have to be formulated in the language of computational mathematics, that is, realizing the importance of computerization of this research field. At the same time it is also important to reveal the “chemical structure” of the explosion limit *via* the numerical definition of the role of individual steps and species of a chain process.

5.4.1. Theoretical Prerequisites of *Value* Analysis of Critical Phenomena in Branching Chain Reactions

Consideration of the critical state of a chain reaction as a process is the specific feature of the offered approach [16,23-25]. The explosion limit was interpreted in such a manner earlier [35].

When considering the explosion limit as an evolutional state of the reaction system we thought the calculus of variations to be more appropriate. At that defining the *criterion of the critical state of a reaction system* in a form suitable for calculations is of special importance.

In [16, 23-25] as a *criterion critical state of the reaction system the extremal behavior of the total concentration of reaction species is suggested*. Such a description of the critical state has obvious advantages. It permits to use mathematical tools on finding the extremal conditions of a reaction. It is well-known that such mathematical approaches are well developed. In this case we have used the calculus of variations, namely the Pontryagin method of maximum with *value* identification of species and steps under critical conditions of a reaction. Thus, simultaneously two important tasks are solved:

- The numerical definition of the reaction critical conditions;
- The identification of the “chemical structure” (role of steps and species) of the critical state.

Isothermal conditions. Calculational procedure on defining and studying the explosion limits for branching chain reactions consists in writing the kinetic equations of a chain reaction according to the reaction mechanism

$$\frac{dc_i}{dt} = f_i(c_1, c_2, \dots, c_m, k_1, k_2, \dots, k_n), \quad i = 1, 2, \dots, m, \quad c_i(t_0) = c_i^0 \quad (5.15)$$

or

$$\frac{dc_i}{dt} = f_i^+ - f_i^- + S_i, \quad i = 1, 2, \dots, m, \quad c_i(t_0) = c_i^0, \quad (5.16)$$

where c_i is the concentration of the i -th reaction species, k_i is the rate constant of an elementary reaction, S_i is the external source of the i -th reaction species, m is the number of reaction species, f_i^+ , f_i^- are the rates of formation and consumption of the i -th species, respectively.

Expression for the total concentration of reaction species is

$$N = \sum_{i=1}^m c_i.$$

From (5.16) we have

$$\frac{dN}{dt} = \sum_{i=1}^m \frac{dc_i}{dt} = \sum_{i=1}^m (f_i^+ - f_i^-) + S, \quad (5.17)$$

$$\text{where } S = \sum_{i=1}^m S_i.$$

Let us formalize the critical state of a reaction system proceeding from its definition, that is, the critical state of a reaction system is extremely related to variations of the kinetic parameters, i.e. $\delta N(t) = 0$, which is equivalent to the target condition

$$I(t) = \int_0^t \frac{dN}{dt} dt \rightarrow \text{extremum.} \quad (5.18)$$

When consumption and formation of molecular particles are negligible, there is nothing to be done than using the total concentration of chain carriers (N_{ac}). So the target function may be presented as

$$I(t) = \int_0^t \frac{dN_{ac}}{dt} dt \rightarrow \text{extremum.} \quad (5.19)$$

Let us write the expression for the appropriate Hamiltonian marking out the parameters Φ by which the critical states of reactions are searched. The initial pressure, temperature, concentrations of species, etc. may serve as such parameters

$$H = \psi_0 f_0 + \sum_{i=1}^m \psi_i f_i(\mathbf{c}, \mathbf{k}, \Phi) \quad (5.20)$$

where $f_0 = dN/dt$ or dN_{ac}/dt , $\psi_0 = 1$ or -1 when the extremum implies maximum or minimum, respectively; ψ_i is the conjugate function of the concentration c_i

$$\frac{d\psi_i}{dt} = -\frac{dH}{dc_i}, \quad i = 1, 2, \dots, m. \quad (5.21)$$

As mentioned in Chapter 4, the highest zero value of the Hamiltonian fits to the extremality conditions (5.18) and (5.19) in the calculus of variations

$$H(\mathbf{c}^*, \psi^*, \Phi^*) = \sup_{\Phi} H(\mathbf{c}, \psi, \Phi) = 0 \quad (5.22)$$

At such problem definition initial characteristics of the reaction system, Φ , act as control parameters.

The condition (5.22) conceptually represents an equation describing the explosion limit that is the critical state of a reaction system.

По существу при вариационном принципе определения the value of characterizes critical conditions of a branching chain reaction, Φ^* представляется как

The value of Φ^* characterizes critical conditions of a branching chain reaction, and the *value* quantities ψ^* characterize the role of reaction individual species under the critical state. According to equations (5.15) and (5.21) based on ψ^* quantities the *values* of individual kinetic steps are identified.

As we have already mentioned, one of the basic advantages of the offered approach is namely in the ability of revealing the chemism of critical phenomena via the *value* quantities. We believe this will allow to specify the effective tools and ways for influencing on the critical conditions of chain reactions.

Nonisothermal conditions. If thermal factors are of considerable importance the system of kinetic equations (5.16) is solved together with the equation describing the temperature variation of the reaction system. As this takes place, the target functional of the calculus of variations is chosen with regard to the temperature factor

$$I(t) = \int_0^t \frac{d(NT)}{dt} dt \rightarrow \text{extremum.} \quad (5.23)$$

It is easy to see that in the functional the quantity NT correlates with the system pressure and the latter is equivalent to the condition $\delta P = 0$.

According to condition (5.23) the equation for the explosion limit is derived from the following system of equations:

$$\begin{cases} \frac{dc_i}{dt} = f_i \\ c_v \rho \frac{dT}{dt} = Q^+ - Q^- = \sum_j q_j r_j + \frac{\chi S}{V} (T - T_a) \quad (\text{energy balanse}) \\ \frac{d\psi_i}{dt} = -\frac{\partial H}{\partial c_i}, \end{cases} \quad i = 1, 2, \dots, m \quad (5.24)$$

where T, P, S and V are the temperature, pressure, surface and the volume of the reactor, respectively; c_v, ρ are the specific heat capacity and density of the reaction system; Q^+, Q^- are the rates of heat release of the chemical reaction and the heat removal from the reaction system, respectively; q_j and r_j are the exothermicity and rate of the j -th reaction step, χ is the heat transfer coefficient, T_a is the ambient temperature. Here a Newtonian cooling through the walls is assumed.

In this case the appropriate Hamiltonian is

$$H = \psi_0 \frac{d(NT)}{dt} + \sum_{i=1}^{m+1} \psi_i f_i(\mathbf{c}, \mathbf{k}, \Phi), \quad (5.25)$$

The condition $i=m+1$ corresponds to the temperature of a reaction system. In fact the temperature is involved in the Hamiltonian as an individual “chemical” species.

Here the task also comes to finding the Φ magnitude for which when solving the equation system (5.24) the corresponding Hamiltonian (5.25) takes its extremum (the condition 5.22). When Φ^* magnitude is not limited, then according to the principle of maximum the Φ^* corresponding to the critical state of a reaction system may be determined from

$$\frac{\partial H}{\partial \Phi_k} = 0, \quad k = 1, 2, \dots, q. \quad (5.26)$$

5.4.2. Illustrative Examples for Studying the Critical State of the Branching Chain Reaction

Let us illustrate the capabilities of the offered method for simple mechanisms of branching chain reactions [1].

- 1. One-centered description of branching chain reaction with linear conversions.** Let us write the appropriate target functional of the calculus of variations for the case under study:

$$I(t) = \int_0^t \frac{dn}{dt} dt \rightarrow \text{extremum} , \quad (5.27)$$

where n is the concentration of chain carriers derived from the equation

$$\frac{dn}{dt} = \varphi \cdot n + S , \text{ where } \varphi = f - g , \quad (5.28)$$

f and g are the kinetic factors for the chain branching and breaking stages, respectively.

Bearing in mind that the explosion limit is described by the equation $\sup H=0$, and the concentration limit meets the condition $\partial H / \partial n = 0$, then, taking into account also (5.20) and (5.28), we have

$$H = \psi_0 \frac{dn}{dt} + \psi \frac{dn}{dt} = (\psi_0 + \psi)(\varphi n + S) = 0 , \quad (5.29)$$

where $\psi_0 = +1$ or -1 .

At the same time, according to (5.21), and taking into account (5.28), we obtain

$$\frac{d\psi}{dt} = -\frac{\partial H}{\partial n} = -\varphi(\psi + \psi_0) , \quad (5.30)$$

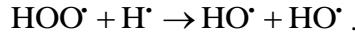
It is easy to verify that for arbitrary ψ the condition $\varphi = 0$ fits the classic extremum condition $\partial H / \partial n = 0$. This latter is the equation specifying the explosion limit for the one-centered problem (see Chapter 1).

- 2. One-centered description of the branching chain reaction with positive interaction of chains.** When positive interaction of chains occurs, the rate of change in the concentration of chain carriers is described by the following equation:

$$\frac{dn}{dt} = bn^2 - |\varphi|n + S , \quad (5.31)$$

where b is the kinetic parameter characterizing the positive interaction of chains. Such a process may occur, for example, at the reaction between hydrogen and oxygen when the relatively passive (for this reaction) hydroperoxy radical HOO^\bullet

reacts with the chain carrier, H^\cdot atom, thus yielding two reactive chain carriers, HO^\cdot hydroxyl radicals



Let us write the equation for the explosion limit to which corresponds the extremum of the target function (5.27)

$$H = (\psi + \psi_0) \frac{dn}{dt} = 0. \quad (5.32)$$

From equation (5.21) we have

$$\frac{d\psi}{dt} = -\frac{\partial H}{\partial n} = -(2bn - |\phi|)(\psi + \psi_0), \quad (5.33)$$

From the extremum condition $\sup H = 0$ according to (5.33) we obtain

$$\frac{dn}{dt} = 0. \quad (5.34)$$

The concentration of chain carriers corresponding to the extremum of Hamiltonian is determined from the classical extremum condition $\partial H / \partial n = 0$. Then, according to (5.33)

$$|\phi| = 2bn, \quad (5.35)$$

So, based on (5.31), (5.34) and (5.35) we have the condition for the explosion limit [1]

$$|\phi| = 2\sqrt{bS}, \quad (5.36)$$

3. **Thermal ignition.** For the problem set it is assumed that $f_i = 0$, $i = 1, 2, \dots, m$. According to (5.25), to the thermal explosion limit $\sup H = 0$ the following condition is relevant

$$\frac{dT}{dt} = 0 \text{ or } Q^+ = Q^-, \quad (5.37)$$

that is, there is an equality between the rates of chemical heat release and heat removal from the reaction system.

At the same time the temperature fitting to the extremum of the Hamiltonian H , according to the classical theory of the calculus of variations, is determined from the condition

$$\partial H / \partial T = 0 ,$$

hence, taking into account equations (5.24) and (5.25), we have

$$\frac{\partial Q^+}{\partial T} = \frac{\partial Q^-}{\partial T} , \quad (5.38)$$

Equations (5.37) and (5.38) constitute the condition for the thermal explosion limit of a reaction mixture [1].

4. **Multicentricity case.** Let us consider the rather simplified scheme of a branching chain reaction by the example of the reaction between hydrogen and oxygen, which is a traditional subject of investigations [1-3].

The corresponding kinetic equations are

$$\begin{aligned} \frac{dc_1}{dt} &= k_2 c_3 c_6 - k_3 c_1 c_5 + k_4 c_2 c_6 - k_5 c_1 - k_6 c_1 c_5 c_M - k_7 c_1 c_4 , \\ \frac{dc_2}{dt} &= k_3 c_1 c_5 - k_4 c_2 c_6 , \\ \frac{dc_3}{dt} &= 2k_1 c_5 c_6 - k_2 c_3 c_6 + k_3 c_1 c_5 + k_4 c_2 c_6 + 2k_7 c_1 c_4 , \\ \frac{dc_4}{dt} &= k_6 c_1 c_5 c_M - k_7 c_1 c_4 , \\ \frac{dc_5}{dt} &= -k_1 c_5 c_6 - k_3 c_1 c_5 - k_6 c_1 c_5 c_M , \\ \frac{dc_6}{dt} &= -(k_1 c_5 + k_2 c_3 + k_4 c_2) c_6 + \frac{1}{2} k_5 c_1 , \\ \frac{dc_7}{dt} &= k_2 c_3 c_6 . \end{aligned} \quad (5.39)$$

Here c_i ($i=1,2,\dots,7$) express the concentration of reaction species $\text{H}\cdot, \text{O}\cdot, \text{HO}\cdot, \text{HOO}\cdot, \text{O}_2, \text{H}_2, \text{H}_2\text{O}$; k_j are the rate constants of individual steps.

The extremality condition is written as

$$I(t) = \int_0^t \frac{dN_{\text{ac}}}{dt} dt = \int_0^t \left(\frac{dc_1}{dt} + \frac{dc_2}{dt} + \frac{dc_3}{dt} + \frac{dc_4}{dt} \right) dt \rightarrow \min . \quad (5.40)$$

Table 5.2. Kinetic model of the reaction between hydrogen and oxygen

No	Steps	Rate constants*
1	$\text{H}_2 + \text{O}_2 \rightarrow 2\text{HO}^\cdot$	$1.5 \cdot 10^{-24}$
2	$\text{HO}^\cdot + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}^\cdot$	$5.53 \cdot 10^{-15}$
3	$\text{H}^\cdot + \text{O}_2 \rightarrow \text{HO}^\cdot + \text{O}^\cdot$	$1.88 \cdot 10^{-15}$
4	$\text{O}^\cdot + \text{H}_2 \rightarrow \text{HO}^\cdot + \text{H}^\cdot$	$3.87 \cdot 10^{-17}$
5	$\text{H}^\cdot \xrightarrow{\text{wall}} 1/2\text{H}_2$	2.26
6	$\text{H}^\cdot + \text{O}_2 + \text{M} \rightarrow \text{HOO}^\cdot + \text{M}$	$1.19 \cdot 10^{-32}$
7	$\text{HOO}^\cdot + \text{H}^\cdot \rightarrow 2\text{HO}^\cdot$	$1.05 \cdot 10^{-10}$

* Rate constants are calculated at $T=423^\circ\text{C}$ in units of number of particles, cm, s.

And the appropriate Hamiltonian takes the form:

$$H = \psi_0 \frac{dN_{\text{ac}}}{dt} + \sum_{i=1}^7 \psi_i f_i = \sum_{j=1}^7 G_j r_j, \quad \psi_0 = -1.$$

In view of the selected target functional (5.40) this equation may be transformed into

$$H = \sum_{j=1}^7 G_j r_j \quad (5.41)$$

According to (5.20) and (5.22) the condition

$$\sum_{j=1}^7 G_j r_j = \sum_{j=1}^7 h_j = 0, \quad (5.42)$$

fits the critical transition, where the step *values* in the given critical state are defined as

$$\begin{aligned}
 G_1 &= 2(\psi_3 - 1) - \psi_5 - \psi_6, \\
 G_2 &= \psi_1 + \psi_7 - \psi_3 - \psi_6, \\
 G_3 &= \psi_2 + \psi_3 - \psi_1 - \psi_5 - 1, \\
 G_4 &= \psi_1 + \psi_3 - \psi_2 - \psi_6 - 1, \\
 G_5 &= 1/2 \psi_6 - \psi_1 + 1, \\
 G_6 &= \psi_4 - \psi_1 - \psi_5,
 \end{aligned} \quad (5.43)$$

$$G_7 = 2\psi_3 - \psi_1 - \psi_4.$$

Solving numerically the system, which includes the kinetic equations (5.39) and equations for conjugate functions (5.21), besides meeting the extremality condition (5.40), and keeping track of the optimum “behavior” of the Hamiltonian by condition (5.22) it is possible to determine the initial pressure corresponding to the condition (5.40), that is, the critical condition of the reaction mixture. Then, using the conjugate functions calculated by equations (5.43) the *values* of individual steps corresponding to the reaction critical state are determined.

The initial $\psi_i(t_0)$ *values* necessary to integrate the equations (5.39) and (5.21) are determined from (5.14) and (5.40)

$$\psi_1(0) = \psi_2(0) = \psi_3(0) = \psi_4(0) = 1, \quad \psi_5(0) = \psi_6(0) = \psi_7(0) = 0.$$

The concentration ratio for initial reagents is as follows: $c_5(0) : c_6(0) = 1 : 2$.

As may be seen from the data of Table 5.3 the reactions 3 and 5 (for chain branching and breaking, respectively) are prevailing on the first explosion limit of the reaction between hydrogen and oxygen. This result is fully natural for the selected sufficiently simple kinetic model of the branching chain reaction [1,2,26].

Calculations have also confirmed the well-known result according to which the reaction (5), for the homogeneous termination of hydrogen atoms, contributes significantly in the second limit of the explosion apart from the chain branching step. At 423°C the following initial pressure values were obtained for the first and second limits of explosion:

$$P_1 = 0.14 \text{ torr}, \quad P_2 = 18.01 \text{ torr}.$$

In this case two of the initial pressures of the reaction mixture, P , corresponded to the zero (extremum) value of the Hamiltonian.

It is of interest to compare the pressure for the first and second limits of explosion derived from the same reaction model with those derived from equations for the one-centered kinetics of the branching-chain reactions [1]

$$P_1 = \frac{1.5k_5}{k_3} = 0.10 \text{ torr}, \quad P_2 = \frac{2k_3}{k_6} = 18.06 \text{ torr}.$$

Slightly overestimated P_1 as compared with the pressure calculated on the basis of the one-centered approach may be conditioned by: (i) the approximation related to the application of the partial stationarity method by concentrations of chain carriers; (ii) the consumption of the initial reagents when reaching the first explosion limit.

Calculations have also shown, if the initial mixture contains some amount of HOO^{\bullet} radicals, then contribution of step (7) in the second limit of explosion increases considerably. So,

$$h_7 / h_3 = 4.35 \cdot 10^{-9} \text{ at } [\text{HOO}^\cdot]_0 = 0,$$

$$h_7 / h_3 = 0.19 \text{ at } [\text{HOO}^\cdot]_0 = 3.22 \cdot 10^{11} \text{ part.} \cdot \text{cm}^{-3}.$$

In this case the pressures for the first and second limits of explosion are:

$$P_1 = 0.14 \text{ torr}, P_2 = 18.5 \text{ torr}.$$

It is worthy of note that deriving explosion limits by the method of the Hamiltonian systematization of dynamic systems is also proved by the example of the reaction between hydrogen and oxygen involving 53 steps [23]. The results obtained are in good agreement with the calculation data of [43], where the extremal behavior of the sensitivity of the maximum concentration of hydrogen atoms relative to the reaction initial conditions is selected as a criterion for the explosion limit.

5. **Degenerate branching-chain reactions.** As presented in Chapter 1, for such reactions the accumulation rate of chain carriers (n) and the intermediate product (P) responsible for the degenerate branching of chains is described by the following equations [51]:

$$\begin{cases} \frac{dn}{dt} = r^0 + fP - gn, \\ \frac{dP}{dt} = an - cP, \end{cases} \quad (5.44)$$

where a , g , and c are the kinetic factors for chain propagation, termination stages and conversion of P, respectively; f is the kinetic factor for the formation of chain carriers from the intermediate product P; r^0 is the rate of chain carrier initiation with participation of the initial substances.

The extremum condition specifying the critical state of a reaction system is

$$I(t) = \int_0^t \frac{d(P+n)}{dt} dt \rightarrow \text{extremum.} \quad (5.45)$$

Table 5.3. Values and contributions of individual steps for the stoichiometric reaction mixture of hydrogen with oxygen on the first explosion limit at $t = 1.25 \cdot 10^{-4}$ s and 423°C

j	1	2	3	4	5	6	7
G_j	0	$-1.45 \cdot 10^{-6}$	-1.99	-2.01	2	2	-2
\bar{h}_j	0	$-1.1 \cdot 10^{-2}$	-1.11	$-2.2 \cdot 10^{-3}$	1.09	$2.56 \cdot 10^{-2}$	$-1.37 \cdot 10^{-17}$

According to (5.44) and (5.45) the appropriate Hamiltonian equals to:

$$H = \psi_0 f_0 + \sum_{i=1}^m \psi_i f_i = (\psi_0 + \psi_n) \frac{dn}{dt} + (\psi_0 + \psi_p) \frac{dP}{dt} = (\psi_0 + \psi_n) r^0 + (\psi_0 + \psi_n) f P - (\psi_0 + \psi_n) g n + (\psi_0 + \psi_p) a n - (\psi_0 + \psi_p) c P, \quad (5.46)$$

where $\psi_0 = +1$ or -1 , $f_0 = d(P + n)/dt$.

At constant a , f , g and r^0 the corresponding equations (5.21) for the conjugate functions ψ_i are as follows:

$$\begin{cases} \frac{d\psi_n}{dt} = -\frac{\partial H}{\partial n} = g(\psi_0 + \psi_n) - a(\psi_0 + \psi_p) \\ \frac{d\psi_p}{dt} = -\frac{\partial H}{\partial P} = c(\psi_0 + \psi_p) - f(\psi_0 + \psi_n) \end{cases} \quad (5.47)$$

The conditions $\partial H / \partial n = 0$ and $\partial H / \partial P = 0$ correspond to the classical extremum condition (5.45). Then from (5.47) we obtain the system of the algebraic equations:

$$\begin{cases} g(\psi_0 + \psi_n) - a(\psi_0 + \psi_p) = 0 \\ c(\psi_0 + \psi_p) - f(\psi_0 + \psi_n) = 0 \end{cases} \quad (5.48)$$

The solution of the equation system (5.48) leads to:

$$\begin{cases} (\psi_0 + \psi_p)(fa - gc) = 0 \\ (\psi_0 + \psi_n)(fa - gc) = 0. \end{cases} \quad (5.49)$$

For arbitrary ψ_n and ψ_p , using (5.49) we have:

$$(fa - gc) = 0 \text{ or } \varphi = \frac{fa}{g} - c = 0. \quad (5.50)$$

The condition (5.50) corresponds to the critical state of the degenerate branching-chain reaction and coincides with (1.20) given in Chapter 1.

6. ***Numerical identification and analysis of critical conditions for liquid-phase oxidation of ethylbenzene inhibited by butylated hydroxytoluene.*** The critical phenomena are studied and analyzed in detail for the liquid-phase autoxidation of organic substances, the carbochain polymers in the presence of inhibitors [32-34,52]. Investigations in this direction currently are also urgent for predicting the antioxidant activity of compounds, including the bioantioxidants [53-67].

As shown earlier, as an indicator of the critical behavior for a reaction system serves the fact that at certain conditions minor increase in the inhibitor concentration ($\Delta[\text{In}]/[\text{In}] \ll 1$) results in the substantial deceleration of reaction or growth in the induction period of reaction (Figure 5.4). Concentration of the inhibitor provoking a change in the reaction mode is defined as critical, $[\text{In}]_{\text{cr}}$.

Knowledge of the reaction regime is of practical importance. As may be seen from Figure 5.4 at concentrations exceeding $[\text{In}]_{\text{cr}}$ the efficiency of the inhibitor is significantly higher. Besides, as will be shown below, identification of the reaction regime is one of the crucial stages facing the selection of an efficient inhibitor for the degenerate branching-chain reactions.

The reasons of critical phenomena in the inhibited liquid-phase oxidation of organic compounds are thoroughly studied. On the basis of theoretical fundamentals of degenerate branching-chain reactions developed by N.N. Semenov [1], N.M. Emanuel and A.B. Gagarina [33] explained the features of the manifestation of critical phenomena in such systems.

Development of universal methods describing the critical phenomena in degenerate branching-chain reactions formulated in the language of computational mathematics, by analogy with the branching-chain reactions, are numbered among the issues of the day. The numerical *value* method for identification and analysis of critical phenomena in degenerate branching-chain reactions is demonstrated by the example of ethylbenzene oxidation inhibited by the orthosubstituted phenol, 2,6-*tert*-butyl-4-methylphenol (butylated hydroxytoluene, BHT). The mechanism for this reaction is interpreted in detail in Chapter 7, and the kinetic model is presented in Table 5.4 [51].

Rate constants for steps 5 and 6 were varied to approach the conditions at which the critical phenomena were observed experimentally, depending on the initial concentration of the inhibitor [33].

To improve the calculation sensitivity with respect to the reaction critical conditions the sum of concentrations change for the initial reagents (with the plus sign) and intermediate products (with the minus sign) was selected as a target functional, excluding oxygen the concentration for which was maintained constant,

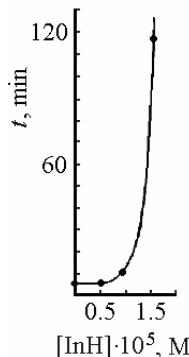
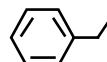


Figure 5.4. Induction period *vs.* concentration of *N*-phenyl- β -naphthylamine in the reaction of ethylbenzene oxidation catalyzed by cobalt (II) acetate ($1.13 \cdot 10^{-2} \text{M}$) at 60°C . Data by [52].

$$I(t) = \Delta[\text{RH}] + \Delta[\text{InH}] - \Delta[\text{R}^\cdot] - \Delta[\text{ROO}^\cdot] - \Delta[\text{RO}^\cdot] - \Delta[\text{ROOH}] - \Delta[\text{In}^\cdot] = \\ = \int_0^t (f_{\text{RH}} + f_{\text{InH}} - f_{\text{R}^\cdot} - f_{\text{ROO}^\cdot} - f_{\text{RO}^\cdot} - f_{\text{ROOH}} - f_{\text{In}^\cdot}) dt \rightarrow \text{extremum} \quad (5.51)$$

RH denotes ethylbenzene



InH denotes butylated hydroxytoluene

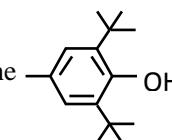
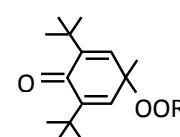
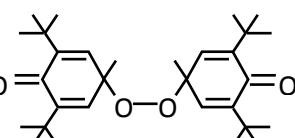
QP₁ denotes asymmetric *para*-quinolide peroxideQP₂ denotes symmetric *para, para*-quinolide peroxide

Table 5.4. Kinetic model for liquid-phase oxidation of ethylbenzene inhibited by butylated hydroxytoluene

N o	Reactions	Rate constants*	
		60 °C	120 °C
1	$2\text{RH} + \text{O}_2 \rightarrow 2\text{R}^\cdot + \text{H}_2\text{O}_2$	$9.26 \cdot 10^{-13}$	$7.7 \cdot 10^{-10}$
2	$\text{R}^\cdot + \text{O}_2 \rightarrow \text{ROO}^\cdot$	$8.75 \cdot 10^8$	10^9
3	$\text{ROO}^\cdot + \text{RH} \rightarrow \text{ROOH} + \text{R}^\cdot$	2.74	39
4	$\text{RO}^\cdot + \text{RH} \rightarrow \text{ROH} + \text{R}^\cdot$	$2.32 \cdot 10^6$	$5.85 \cdot 10^6$
5	$\text{ROOH} + \text{RH} \rightarrow \text{RO}^\cdot + \text{R}^\cdot + \text{H}_2\text{O}$	$1.28 \cdot 10^{-5}$ or 10^{-3}	$1.28 \cdot 10^{-5}$ or 10^{-3}
6	$\text{ROOH} + \text{RH} \rightarrow \text{R}(-\text{H})\text{O} + \text{RH} + \text{H}_2\text{O}$	$1.28 \cdot 10^{-4}$ or 10^{-2}	$1.28 \cdot 10^{-4}$ or 10^{-2}
7	$\text{ROO}^\cdot + \text{ROO}^\cdot \rightarrow \text{RO}^\cdot + \text{RO}^\cdot + \text{O}_2$	$5.5 \cdot 10^6$	10^7
8	$\text{ROO}^\cdot + \text{ROO}^\cdot \rightarrow \text{ROH} + \text{R}(-\text{H})\text{O} + \text{O}_2$	10^7	$3.5 \cdot 10^7$
9	$\text{ROO}^\cdot + \text{InH} \rightarrow \text{ROOH} + \text{In}^\cdot$	$2.04 \cdot 10^4$	$6.94 \cdot 10^4$
10	$\text{In}^\cdot + \text{In}^\cdot \rightarrow \text{InH} + \text{In}(-\text{H})$	$1.1 \cdot 10^4$	$3.3 \cdot 10^4$
11	$\text{In}^\cdot + \text{ROO}^\cdot \rightarrow \text{QP}_1$	$3 \cdot 10^8$	$3 \cdot 10^8$
12	$\text{ROOH} + \text{InH} \rightarrow \text{In}^\cdot + \text{RO}^\cdot + \text{H}_2\text{O}$	$1.75 \cdot 10^{-7}$	$6.7 \cdot 10^{-5}$
13	$\text{ROOH} + \text{In}^\cdot \rightarrow \text{InH} + \text{ROO}^\cdot$	1	15.23
14	$\text{In}^\cdot + \text{In}^\cdot + \text{O}_2 \rightarrow \text{QP}_2$	$4.9 \cdot 10^3$	$4.9 \cdot 10^3$

* Rate constants are given in the units M, s.

Let us write the initial conditions required for solving the system of canonical equations (5.15) and (5.21). According to the target functional (5.51) the initial values for conjugate functions are as follows:

$$\begin{aligned}\psi_{RH}(0) &= \psi_{InH}(0) = 1 \\ \psi_{R\cdot}(0) &= \psi_{ROO\cdot}(0) = \psi_{RO\cdot}(0) = \psi_{ROOH}(0) = \psi_{In\cdot}(0) = 1 \\ \psi_{O_2}(0) &= \psi_{H_2O_2}(0) = \psi_{H_2O}(0) = \psi_{ROH}(0) = \psi_{R(-H)O}(0) = 0 \\ \psi_{In(-H)O}(0) &= \psi_{QP_1}(0) = \psi_{QP_2}(0) = 0\end{aligned}$$

with the initial concentrations for reaction species: $[RH]_0=7.8$ M; $[O_2]_0=10^{-2}$ M=const; $[ROOH]_0=10^{-6}$ M (initial concentrations for other reaction species equal to zero).

In accordance with the procedure described above, let us determine the initial concentration of the inhibitor at which the extremality condition (5.51) and the reaction critical condition (5.22) are observed simultaneously when the system of canonical equations (5.15) and (5.21) is solved numerically at the selected initial values of $\psi_i(0)$ and c^0 .

Dependences for the calculated induction period and the Hamiltonian of the reaction system on the initial inhibitor concentration are illustrated in Figure 5.4. The induction period was calculated as the time required to reach 0.01% conversion of the hydrocarbon corresponding to the time of practically full conversion (more than 99.9%) of the inhibitor.

Figure 5.5 clearly demonstrates the critical phenomena: there exists an initial concentration of the inhibitor resulting in drastic constant of step 5 (degenerate branching of the chain) the more clearly expressed the critical phenomena. This is in compliance with the accepted theoretical conceptions for such processes [33]. It should be reminded that according to the selected criterion for the case under consideration the minimum of the Hamiltonian (extremality condition 5.22) corresponds to the critical state of the reaction system.

It follows from the computed data presented in Figure 5.5 that the critical initial concentrations of the inhibitor fitting the minimum of the Hamiltonian, precisely predict these critical concentrations identified from the dependency of the induction period on the initial concentration of the inhibitor.

It should be emphasized particularly that such agreement is obtained for a quite complicated reaction mechanism and under conditions when the inhibitor is continuously consuming during the induction period by which the critical behavior of the reaction system is examined. This factor usually complicates the task of defining the critical initial concentration of the inhibitor [32, 33]. The problem remains also when using other methods to determine the instability of reaction systems.

Evidently, determination of reaction critical conditions by the extremum of the Hamiltonian is substantially simpler as it requires too little scope of computing and consequently expenditure of time. According to inferences of the calculus of variations

$$H(t) = \text{const.}$$

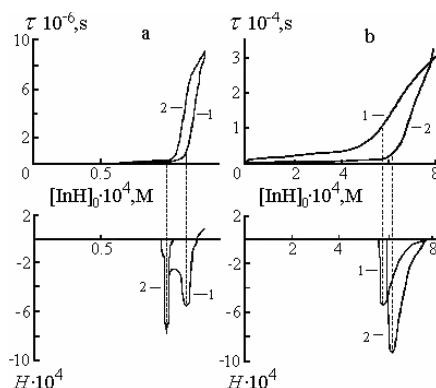
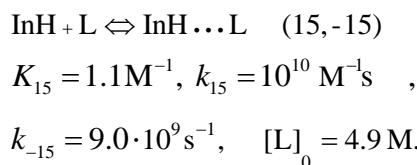


Figure 5.5. Calculated dependences for the Hamiltonian (H) and induction period (τ) at ethylbenzene oxidation inhibited by butylated hydroxytoluene at temperatures 60 °C (a) and 120 °C (b). $[RH]_0 = 7.8$ M; $[ROOH]_0 = 10^{-6}$ M; $[O_2] = 10^{-2}$ M = const. Calculations were carried out at $k_5 = 1.28 \cdot 10^{-5}$ M $^{-1}$ s $^{-1}$ (1); $k_5 = 10^{-3}$ M $^{-1}$ s $^{-1}$ (2); and $k_5/k_6 = 0.1$. Dashed lines correspond to critical concentrations of the inhibitor $[InH]_{cr}$.

For this reason the extremum of the Hamiltonian for a reaction system may be determined at significantly short reaction times using special algorithms. This facilitates computational procedures.

It is of interest to compare the calculation data for $[InH]_{cr}$ with experimental results. At 60 °C and $[RH]_0 = 3.24$ M we calculated $[InH]_{cr}^{\text{calc}} = 4.1 \cdot 10^{-5}$ M, while under the same conditions the liquid-phase oxidation of ethylbenzene catalyzed by cobalt (II) acetate gives $[InH]_{cr}^{\text{exp}} = 2.75 \cdot 10^{-4}$ M [33]. This discrepancy may be related to the fact that in experiments acetic acid was used as the reaction medium. The latter in turn decreases considerably the rate constant for the reaction between the peroxy radical and the phenolic inhibitor due to the formation of the intermolecular hydrogen bond between the solvent and the phenyl OH-group of butylated hydroxytoluene [59-61], that causes growth in $[InH]_{cr}^{\text{exp}}$. To check this assumption the reaction scheme in the Table was supplemented with steps taking into account the equilibrium formation of the intermolecular hydrogen bond between the phenyl OH-group of BHT and the molecule of acetic acid (L):



In this case it is taken into account that the complex with intermolecular hydrogen bond ($InH \dots L$) does not possess antiperoxyradical activity [59-61]. The rate constants for steps (15) and (-15) were estimated based on considerations that the equilibrium constant (K_{15}) at 60 °C is equal to 1.1 M $^{-1}$ and this value is close to that for the bimolecular diffusion-controlled reaction.

Taking into account the equilibrium (15,-15) the value of $[\text{InH}]_{\text{cr}} = 2.83 \cdot 10^{-4} \text{ M}$ was determined. Therefore, involving this equilibrium improves substantially the convergence of calculated and experimental data.

Numerical calculation of the value contributions of individual steps of the kinetic model. As mentioned above, parametric corollaries of the Hamiltonian systematization of reaction systems, namely, the *value* contributions of steps specify their kinetic significance.

Therefore, the calculated *value* contributions for individual steps (h_i) corresponding to the critical conditions of the reaction seems to contain highly valuable information.

Value ranking of individual steps illustrated in Figure 5.6 makes it possible to select the steps that play a dominant role under the critical conditions of the degenerate branching-chain reaction:

step 1 - chain initiation; step 3 – rate-limiting step of chain propagation; step 5 – degenerate branching of the chain; steps 9 and 11 - chain breaking with participation of the inhibitor. At high temperatures (120°C) the chain transfer (13) with participation of the inhibitor's radical is of primary importance.

Value analysis of kinetic models also enables to determine the insignificant steps and remove them from the reaction scheme without any “harm” in the accuracy (less than 3%) of the $[\text{InH}]_{\text{cr}}$ calculation. Steps 7, 12 and 14 for which $\bar{h}_j < 10^{-7}$ have been identified as redundant.

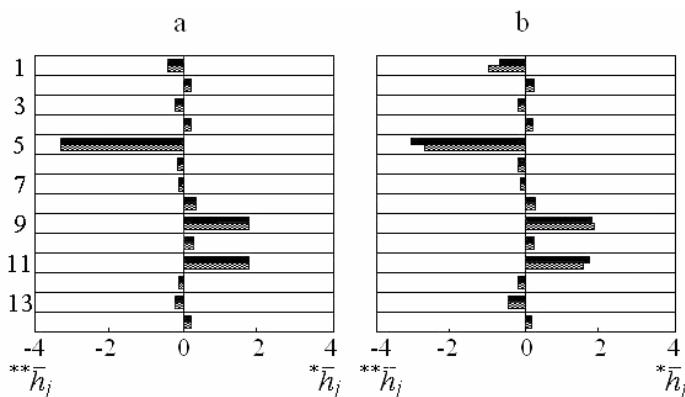


Figure 5.6. Reduced *value* contributions of individual steps for liquid-phase oxidation of ethylbenzene inhibited by butylated hydroxytoluene at conversions of the inhibitor 0.1% and 0.37% and temperatures 60°C (a) and 120°C (b). The initial concentrations of the inhibitor correspond to the critical magnitudes: $[\text{InH}]_{\text{cr}}^{60^{\circ}\text{C}} = 1.2 \cdot 10^{-4} \text{ M}$; $[\text{InH}]_{\text{cr}}^{120^{\circ}\text{C}} = 3.9 \cdot 10^{-4} \text{ M}$; and

$[\text{RH}]_0 = 7.8 \text{ M}$; $[\text{ROOH}]_0 = 10^{-6} \text{ M}$; $[\text{O}_2] = 10^{-2} \text{ M} = \text{const}$; $k_5 = 1.28 \cdot 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$. For the sake of obviousness the reduced *value* contributions of steps are presented after an appropriate transformation by the formulae ${}^* \bar{h}_j = -(\lg |\bar{h}_j|)^1$; ${}^{**} \bar{h}_j = (\lg |\bar{h}_j|)^1$.

The autoinitiation step 12 including hydroperoxide and inhibitor molecules, along with reaction 13 of the chain transfer with participation of inhibitor's radical, In^\cdot , usually plays an important role in the antioxidant protection of organic substrates (see, for example, [62-67]). In the discussed example the role of these steps, especially at 60°C is weakly expressed because of the high rate constant of step 5 (degenerate chain branching) at which the critical phenomena are expressed more clearly. In fact, in this case the degenerate chain branching step occurs with relatively intensive "screens" pro-oxidant properties of the antioxidant, presented in the considered case by steps 12 and 13. Nevertheless, step 12 may be accelerated considerably in the presence of catalytic amounts of metal ions [65]. Then its role will be substantial.

Thus, it may be concluded that the offered *value* method makes it possible to calculate explosion limits and critical parameters irrespective of the complexity of the mechanism of the branching-chain reaction. Simultaneously, by means of *value* ranking of steps it becomes possible to interpret in "chemical" terms the critical state of a reaction system.

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Chapter 6

ILLUSTRATIVE EXAMPLES OF *VALUE* ANALYSIS APPLICATION FOR CHEMICAL REACTION CONTROL

The illustrative examples of the application of *value* analysis for the kinetic models of reactions are considered for their optimal control. The first example shows a degenerate-branching chain reaction for the oxidation of benzaldehyde by dioxygen. The selected target condition characterizes the maximum selectivity of perbenzoic acid formation. The *value* analysis revealed the way of efficient controlling this reaction. In particular, it is predicted that the increase in the rate of steps for degenerate-branching and propagation of chains by means of catalysts leads to a significant increase in the yield of the target product, the perbenzoic acid.

Value analysis has been applied also to the kinetic model for the oxidation of unsaturated aldehyde, α -methylacrolein. As a result an original way is found to increase successfully the yield of target products, α -methyl acrylic and peroxyacrylic acids, by the purposeful suppression (using inhibitors) of free radical chain oxidation reactions involving double bonding. This phenomenon is represented as “selective inhibition of chain reactions”. In this case the inhibitor suppresses not the entire chain process, but selectively impedes the proceeding of its unwanted routes leading to the formation of by-products.

In Chapter 6 we address in detail the following issue: in what way one can successfully and most effectively combine the *value* analysis of kinetic models with the solution of the problem on the optimal control of a chemical reaction. In this Chapter we will consider two examples of chemical reactions. For these reactions the selective transformation of initial reagents into the target products is highly important.

6.1. SELECTIVE LIQUID-PHASE OXIDATION OF BENZALDEHYDE INTO PEROXYBENZOIC ACID

Selection of this reaction is mainly caused by relatively simple reaction mechanism [1]. Here we followed the idea that the simple kinetic reaction models may be solved analytically and full scope or comprehensive analysis may be carried out. Such kinetic models seem to be convenient to demonstrate the capabilities of the offered approach.

Table 6.1. Kinetic model for liquid-phase oxidation of benzaldehyde

No	Steps*	Rate constants
1	$2\text{PhCHO} + \text{O}_2 \rightarrow 2\text{Ph}\dot{\text{C}}\text{O} + \text{H}_2\text{O}_2$	$4 \cdot 10^{-6}$
2	$\text{Ph}\dot{\text{C}}\text{O} + \text{O}_2 \rightarrow \text{PhCO}_3^{\bullet}$	$2 \cdot 10^9$
3	$\text{PhCO}_3^{\bullet} + \text{PhCHO} \rightarrow \text{PhCO}_3\text{H} + \text{Ph}\dot{\text{C}}\text{O}$	$3 \cdot 10^4$
4	$\text{PhCO}_3\text{H} \xrightarrow{\text{cat}} \text{PhCO}_3^{\bullet}$	$3 \cdot 10^{-6}$
5	$\text{PhCO}_3\text{H} + \text{PhCHO} \rightarrow 2\text{PhCO}_2\text{H}$	10^{-4}
6	$\text{PhCO}_3^{\bullet} \xrightarrow{\text{cat}} \text{nonradical products}$	$1.2 \cdot 10^2$

* *Ph* denotes phenyl group, and rate constants are presented at $T = 40^{\circ}\text{C}$ in units of M, s.

Liquid-phase oxidation of benzaldehyde is of the chain nature. One way to illustrate the reaction mechanism in the presence of catalytic additives is the set of steps [2-6] given in Table 6.1.

Liquid-phase oxidation of benzaldehyde belongs to the class of degenerate branching-chain process. In the kinetic model under consideration the degenerate chain branching takes place due to the catalytic decomposition of the formed peroxyacid (step 4). This reaction is also specific, because the nonradical reaction of the formed peroxyacid with the initial benzaldehyde (step 5) is the main channel for the further transformation of the peroxyacid. Here the following reviews should be mentioned [2,5,6] that provide additional information about the mechanism of liquid-phase oxidation of aldehydes.

From the practical standpoint the main goal for this reaction is to achieve the maximum yield of the peroxyacid [3]. In the approximation of steady concentrations of free radicals and provided that high average chain lengths are realized ($r_3 \gg r_6$), and the rate of a degenerate branching step (4) exceeds that of the chain initiation by step (1), from the scheme illustrated in Table 6.1 one can find the following analytical dependence for the selectivity of peroxybenzoic acid (S) on the conversion (K) of the initial benzaldehyde [3]:

$$S = \frac{k_3 k_4 - k_5 k_6}{k_3 k_4 + k_5 k_6} + \frac{k_4 k_5}{(k_3 k_4 + k_5 k_6) [\text{PhCHO}]_0} \cdot \frac{\ln(1 - K)}{K}, \quad (K \neq 0) \quad (6.1)$$

$$S = \frac{[\text{PhCHO}_3\text{H}]_t}{[\text{PhCHO}]_0 - [\text{PhCHO}]_t}; \quad K = \frac{[\text{PhCHO}]_0 - [\text{PhCHO}]_t}{[\text{PhCHO}]_0}.$$

It can be seen from the obtained relationship that steps of propagation (3) and degenerate branching (4) have favorable influence on the reaction selectivity, whereas steps of peroxyacid molecular (nonradical) transformation (5) and chain breaking (6) act negatively. Now let us examine the same mechanism by the *value* method choosing the selectivity as a target functional by analogy with (3.11) (see Chapter 3).

$$I(t) = \Delta[\text{PhCHO}]_t + \Delta[\text{PhCO}_3\text{H}]_t = \int_{t_0}^t (f_{\text{PhCHO}} + f_{\text{PhCO}_3\text{H}}) dt, \quad (6.2)$$

where f_{PhCHO} , $f_{\text{PhCO}_3\text{H}}$ are the rates of benzaldehyde consumption and peroxyacid accumulation, respectively. To reduce the notation let us introduce the following designations:

$$\begin{aligned} c_1 &= [\text{PhCHO}], \quad c_2 = [\text{Ph}\overset{\bullet}{\text{CO}}], \quad c_3 = [\text{H}_2\text{O}_2], \quad c_4 = [\text{PhCO}_3^\bullet], \\ c_5 &= [\text{PhCO}_3\text{H}], \quad c_6 = [\text{PhCO}_2\text{H}], \quad c_7 = [\text{O}_2] = \text{const.} \end{aligned}$$

Then appropriate Hamiltonian according to (3.14) will be as follows

$$H = -f_{\text{PhCHO}} - f_{\text{PhCO}_3\text{H}} + \sum_{i=1}^6 \psi_i f_i. \quad (6.3)$$

The rates of changing the reaction species concentrations are described by a system of differential equations

$$\begin{aligned} \frac{dc_1}{dt} &= -2k_1 c_1^2 c_7 - k_3 c_1 c_4 - k_5 c_1 c_5, \\ \frac{dc_2}{dt} &= 2k_1 c_1^2 c_7 - k_2 c_2 c_7 + k_3 c_1 c_4, \\ \frac{dc_3}{dt} &= k_1 c_1^2 c_7, \\ \frac{dc_4}{dt} &= k_2 c_2 c_7 - k_3 c_1 c_4 + k_4 c_5 - k_6 c_4, \\ \frac{dc_5}{dt} &= k_3 c_1 c_4 - k_4 c_5 - k_5 c_1 c_5, \\ \frac{dc_6}{dt} &= 2k_5 c_1 c_5. \end{aligned} \quad (6.4)$$

The next step is compiling the system of differential equations for conjugate functions according to equation (3.18)

$$\begin{aligned} \frac{d\psi_1}{dt} &= (4k_1 c_1 c_7 + k_3 c_4 + k_5 c_5) \psi_1 - (4k_1 c_1 c_7 + k_3 c_4) \psi_2 - 2k_1 c_1 c_7 \psi_3 + \\ &+ k_3 c_4 \psi_4 - (k_3 c_4 + k_5 c_5) \psi_5 - 2k_5 c_5 \psi_6 - 4k_1 c_1 c_7 - 2k_5 c_1, \\ \frac{d\psi_2}{dt} &= k_2 c_7 \psi_2 - k_2 c_7 \psi_4, \quad \frac{d\psi_3}{dt} = 0, \end{aligned} \quad (6.5)$$

$$\begin{aligned}\frac{d\psi_4}{dt} &= k_3 c_1 \psi_1 - k_3 c_1 \psi_2 + (k_3 c_1 + k_6) \psi_4 - k_3 c_1 \psi_5 - 2k_3 c_1, \\ \frac{d\psi_5}{dt} &= k_5 c_1 \psi_1 - k_4 \psi_4 + (k_4 + k_5 c_1) \psi_5 - 2k_5 c_1 \psi_6 - 2k_5 c_1, \\ \frac{d\psi_6}{dt} &= 0.\end{aligned}$$

Let us adopt the following initial conditions for equations (6.4) and (6.5):

$$\begin{aligned}c_1(0) &= 1 \text{M}, \quad c_7(0) = 0.01 \text{M} = \text{const}, \\ c_2(0) &= c_3(0) = c_4(0) = c_5(0) = c_6(0) = 0.\end{aligned}$$

In accordance with the target functional (6.2)

$$\psi_1(0) = \psi_5(0) = 1, \quad \psi_2(0) = \psi_3(0) = \psi_4(0) = \psi_6(0) = 0.$$

The *values* of steps according to equation (3.5) are expressed through the conjugate functions ψ_i :

$$\begin{aligned}G_1 &= 2\psi_2 + \psi_3 - 2\psi_1 - \psi_7, \\ G_2 &= \psi_4 - \psi_2 - \psi_7, \\ G_3 &= \psi_2 + \psi_5 - \psi_1 - \psi_4, \\ G_4 &= \psi_4 - \psi_5, \\ G_5 &= 2\psi_6 - \psi_1 - \psi_5, \\ G_6 &= -\psi_4.\end{aligned}\tag{6.6}$$

Then calculations by equations (6.4) result in kinetic curves for benzaldehyde consumption and the accumulation of the reaction end products (Figure 6.1). Figure 6.2 illustrates kinetic trajectories of the reduced contributions of individual steps, computed by equations (6.1) – (6.6) for the same conditions

$$\bar{h}_j = h_j \left(\sum_{j=1}^6 h_j^2 \right)^{-1/2}, \quad \text{where } h_j = G_j r_j.\tag{6.7}$$

The results obtained validate the conclusion made on the basis of the analytical solution. Actually, it follows from Figures 6.1 and 6.2 that at detectable conversion of benzaldehyde (for $t > 10^3$ s), steps (3) and (4) promote increasing in the reaction selectivity, while steps (5) and (6) act inversely. In this case there is no necessity to introduce the approximation $r_1 \ll r_4$ to solve the problem. It follows from the kinetic trajectories of contributions for steps (1) and (4) that the higher is the aldehyde conversion the lower is the role of step (1) in free radical

generation, but, at the same time, the higher is the role of degenerate branching step (4). The contribution of steps are identified too for the time interval $t < 10^{-2}$ s, where steady-state condition by the concentration of free radicals is not met. Considerable negative contribution of step (1), generation of free radicals (see Figure 6.2), most likely is conditioned by the following reason. At very low conversion degrees of benzaldehyde (less than 10⁵%) the kinetic chain, yielding the end product, peroxyacid, is not realized and the free radical concentration is commensurable with the concentration of the secondary product PhCO₂H.

Now the problem of optimal control may be solved more strictly by preliminary selecting as control parameters the rate constants for steps (3) and (4), influencing positively on the selectivity. Obviously, by controlling the rate constants of steps it should be understood the application of experimental tools that have an influence upon these parameters, for example, using the appropriate catalysts.

The condition of maximum for the target functional (6.2) fits the problem of optimal control of

$$I(t) = \int_{t_0}^t (f_{\text{PhCHO}} + f_{\text{PhCO}_2\text{H}}) dt \rightarrow \max . \quad (6.8)$$

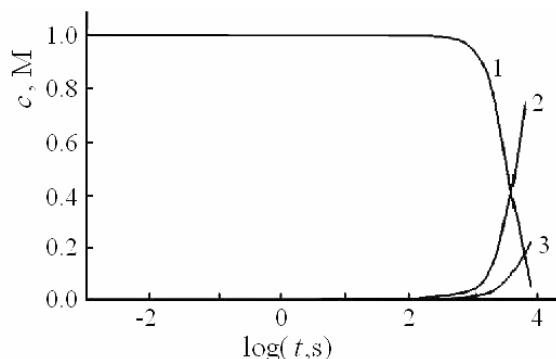


Figure 6.1. Kinetic curves of benzaldehyde consumption (1) and accumulation of peroxybenzoic (2) and benzoic (3) acids.

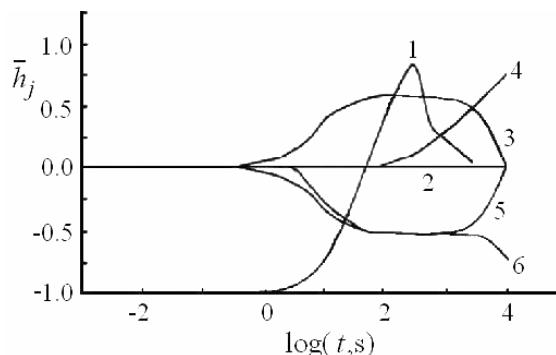


Figure 6.2. Kinetic trajectories of the reduced *value* contributions of individual steps for liquid-phase oxidation of benzaldehyde. The curves are numbered in accordance with the steps.

Further let us impose restrictions on the control variables k_3 and k_4 : the rate constants of chain propagation and degenerate branching, respectively

$$3 \cdot 10^4 \leq k_3 \leq 8 \cdot 10^4 \text{ M}^{-1}\text{s}^{-1},$$

$$3 \cdot 10^{-6} \leq k_4 \leq 3 \cdot 10^{-5} \text{ s}^{-1}.$$

Let us represent the Hamiltonian in an explicit dependence on the control parameters

$$H = \psi_0(f_1 + f_5) + \sum_{i=1}^6 \psi_i f_i. \quad (6.9)$$

When controlling by step (3) the Hamiltonian may be presented as

$$H = \chi_1 + \vartheta_1 k_3, \quad (6.10)$$

where $\vartheta_1 = c_1 c_4 (\psi_2 - \psi_1 - \psi_4 + \psi_5)$

$$\begin{aligned} \chi_1 = & -\psi_0 (k_4 c_5 + 2k_1 c_1^2 c_7 + 2k_5 c_1 c_5) - \psi_1 (2k_1 c_1^2 c_7 + k_5 c_1 c_5) + \\ & \psi_2 (2k_1 c_1^2 c_7 - k_2 c_2 c_7) + \psi_3 k_1 c_1^2 c_7 + \psi_4 (k_2 c_2 c_7 + k_4 c_5 - k_6 c_4) - \\ & - \psi_5 (k_4 c_5 + k_5 c_1 c_5) + 2\psi_6 k_5 c_1 c_5 \end{aligned}$$

When controlling by step (4) the Hamiltonian takes the form

$$H = \chi_2 + \vartheta_2 k_4 \quad (6.11)$$

where $\vartheta_2 = c_5 (\psi_0 + \psi_4 - \psi_5)$,

$$\begin{aligned} \chi_2 = & -2\psi_0 (k_1 c_1^2 c_7 + k_5 c_1 c_5) + \psi_1 (-2k_1 c_1^2 c_7 + k_3 c_1 c_4 - k_5 c_1 c_5) + \psi_2 (2k_1 c_1^2 c_7 - k_2 c_2 c_7 + k_3 c_1 c_4) + \\ & + \psi_3 k_1 c_1^2 c_7 + \psi_4 (k_2 c_2 c_7 - k_3 c_1 c_4 - k_6 c_4) + \psi_5 (k_3 c_1 c_4 - k_5 c_1 c_5) + 2\psi_6 k_5 c_1 c_5 \end{aligned}$$

In the case under consideration the problem is solved with the condition of maximum for the target functional (6.8), therefore $\psi_0 = 1$. Calculations have shown that the ϑ_1 and ϑ_2 values are positive in the considered variation range of the control parameters k_3 and k_4 . At that it is obvious from expressions (6.10) and (6.11) that the Hamiltonian varies linearly, depending on the control parameters. In such case, according to the Pontryagin principle of maximum (see Chapter 4), the maximum values of k_3 and k_4 correspond to that of the target functional and, consequently to the selectivity. Indeed, as it follows from the data presented in Table 6.2, increase in the k_3 and k_4 values results in the increase of the target functional (I) and the reaction selectivity.

Table 6.2. Computed target functional (*I*) and selectivity (*S*) for benzaldehyde oxidation* into peroxybenzoic acid depending on the *k*₃ and *k*₄ magnitudes

<i>k</i> ₃ , M ⁻¹ s ⁻¹	3·10 ⁴	6·10 ⁴	8·10 ⁴
<i>S</i> , mol %	77.3	86.6	89.2
<i>I</i>	0.794	0.867	0.893
<i>k</i> ₄ , s ⁻¹	3·10 ⁻⁶	8·10 ⁻⁶	3·10 ⁻⁵
<i>S</i> , mol %	77.3	86.4	90.5
<i>I</i>	0.794	0.862	0.894

* Conversion of benzaldehyde makes up 93-98%.

6.2. SELECTIVE INHIBITION OF LIQUID-PHASE OXIDATION OF α -METHYLACROLEIN

Similar to benzaldehyde the oxidation of α -methylacrolein is of the chain nature. However, this reaction is described by a considerably more complicated kinetic model, including the set of individual steps [7-9] shown in Table 6.3.

Table 6.3. Reaction mechanism of liquid-phase oxidation of α -methylacrolein

No	Reactions	Rate constants*
1	2RCHO + O ₂ → 2 R \dot{C} O + H ₂ O ₂	4·10 ⁻⁵
2	R \dot{C} O + O ₂ → RCO ₃ [·]	10 ⁹
3	RCO ₃ [·] + RCHO → RCO ₃ H + R \dot{C} O	9.8·10 ²
4	RCO ₃ [·] + RCHO → M [·] + P	1.6·10 ²
5	M [·] + O ₂ → MOO [·]	10 ⁸
6	MOO [·] + RCHO → M [·] + P	60
7	MOO [·] + RCHO → MO ₂ H + R \dot{C} O	4
8	RCO ₃ H → RCO ₂ [·] + HO [·]	5·10 ⁻⁵
9	RCO ₂ [·] + RCHO → RCO ₂ H + R \dot{C} O	10 ⁻⁶
10	HO [·] + RCHO → R \dot{C} O + H ₂ O	7·10 ⁸
11	RCO ₃ H + RCHO → 2RCO ₂ H	2·10 ⁻³
12	RCO ₃ [·] + RCO ₃ [·] → nonradical products	10 ⁸
13	MOO [·] + MOO [·] → nonradical products	10 ⁵
14	MOO [·] + RCO ₃ [·] → nonradical products	10 ⁷
15	RCO ₃ [·] + In → nonradical products	3·10 ⁴
16	MOO [·] + In → nonradical products	3·10 ⁴
17	R \dot{C} O + In → nonradical products	10 ⁴
18	M [·] + In → nonradical products	10 ⁴

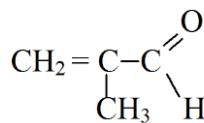
* Rate constants are given at 70 °C [7], in units of M, s.

Detailed review of studies on the auto- and catalytic-oxidation of unsaturated aldehydes in the liquid phase may be found in [2,9]. Here we just note the main specific feature of the unsaturated aldehydes oxidation, briefly cited in Section 5.2. It implies that the free-radical chain process of the aldehyde group oxidation stimulates undesirable reactions, including the copolymerization of aldehyde with oxygen through the aldehyde's double bond, and in some cases also the copolymerization of the reaction products, the unsaturated acids and peroxyacids with oxygen. The oxidation reactions of unsaturated aldehydes are defined as the multicentered chain processes with two types of reaction centers: acyl monomeric and polyperoxide free radicals.

The reactions of chain propagation are presented through steps (2), (3), (7) for the oxidation of the aldehyde group and steps (4), (5) and (6) for the reactions with participation of the double bond.

According to the abovementioned scheme, the formation of polymeric and some low-molecular compounds, decreasing the yield of target products occurs due to the addition of acylperoxyl radicals RCO_3^\bullet to the double bond (step 4), followed by the formation of polyperoxides and the products of the destructive decomposition of carbon-centered polyperoxide radicals. The inhibitor introduced into the reaction mixture participates in the reactions of radical termination (steps 15-18).

In denotes inhibitor; P denotes polyperoxide and products of destructive oxidation of α -methylacrolein (RCHO) with the following molecular structure:



M^\bullet is the carbon-centered polyperoxide radical with a molecular structure shown in Chapter 5. The concentrations of oxygen and the inhibitor were kept constant.

The α -methylacrylic acid and peroxy methylacrylic acids, RCO_2H and RCO_3H , are the target products (tp) of the liquid-phase oxidation.

From a methodical viewpoint it seems practical to address first the possibilities of the selective inhibition of the undesirable direction of the reaction for liquid-phase oxidation of α -methylacrolein, by using the formal kinetic tool for the multicentered chain reactions presented in the Section 5.1. Now, by analogy with the scheme (5.1), we present the above-listed set of steps (1-18) as the flow graph (Figure 6.3) for the multicentered chain process [10].

The condition for the selective inhibition of product formation with the participation of the polyperoxide radicals according to (5.12) may be written as

$$\nu_{\text{RCO}_3^\bullet}^{\text{tp}} > \nu_{\text{MO}_2^\bullet}^{\text{tp}}. \quad (6.12)$$

After some simplifications this condition transforms into the inequality

$$k_{41} < k_4[\text{In}]. \quad (6.13)$$

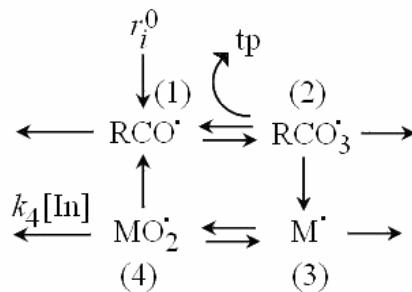


Figure 6.3. Flow graph illustrating the chain oxidation of unsaturated aldehyde.

According to the detailed oxidation scheme, k_{41} and k_4 (see notations in Chapter 5) correspond to $k_7[\text{RCHO}]$ and k_{16} .

For concentrations $[\text{In}] > 2 \cdot 10^{-3}$ M the condition (6.13) and consequently (6.12) are met, indicating the possibility to perform the selective inhibition of the chain liquid-phase oxidation of α -methylacrolein.

As mentioned earlier in Chapter 5, selective inhibition is realized in practice. Introduction of inhibitors into the reaction system enabled to increase the yield of the end product, the α -methylacrylic acid [4,7,8,10].

More rigorous and comprehensive consideration of the possibilities for the selective inhibition in the oxidation of α -methylacrolein may be attained using the *value* approach. In such a case, the selectivity of the α -methylacrolein conversion into the target products, the proper acids, is used as a target functional:

$$I(t) = \int_{t_0}^t (f_{\text{RCHO}} + f_{\text{RCO}_2\text{H}} + f_{\text{RCO}_3\text{H}}) dt. \quad (6.14)$$

The system of differential equations (3.16) and (3.18) (Chapter 3) was solved for the following initial conditions: $[\text{RCHO}]_0 = 1$ M; $[\text{O}_2]_0 = 0.04$ M = const; $[\text{In}]_0 = \text{const}$. Proceeding from the target functional (6.14) we have

$$\psi_{\text{RCHO}}(0) = \psi_{\text{RCO}_2\text{H}}(0) = \psi_{\text{RCO}_3\text{H}}(0) = 1.$$

The calculated kinetic curves (Figure 6.4) for the main reaction species are in good agreement with the experimental data [8].

It follows from the dependency of calculated *value* contributions on the conversion of α -methylacrolein (Figure 6.5) that the *value* contributions of steps (12)-(14), (17) and (18) are very small throughout the process. These steps are the candidates for the exclusion from the reaction scheme, aimed at composing the “base” (reduced) reaction mechanism. The final answer for the actual insignificance of these steps will be available by estimating the response of the reaction system to their sequential exclusion from the reaction scheme. The steps were taken as insignificant if their total excluding from the reaction scheme resulted in deviations in the calculated kinetic curves of the α -methylacrolein consumption and the accumulation of

the α -methylacrylic and peroximethylacrylic acids, to no more than 3%. In this way the steps (12)-(14), (17) and (18) included in Table 6.3 may be considered as redundant and excluded from the reaction scheme.

Calculations have shown that in the conversion range of α -methylacrolein of up to 35% (for $t \leq 10^4$ s) (see also Figure 6.4) the contributions of steps (1) and (8), relevant to free radicals generation are negative, while contributions of steps (15) and (16) on free radicals termination are positive. From this follows the conclusion about the possibility of controlling (in the considered case raising) the selectivity of chain reaction by the stimulation of steps (15, 16) that lead to the termination of free radicals. Calculations carried out also confirm that the introduction of inhibitors leads to the increase in reaction selectivity (Table 6.4).

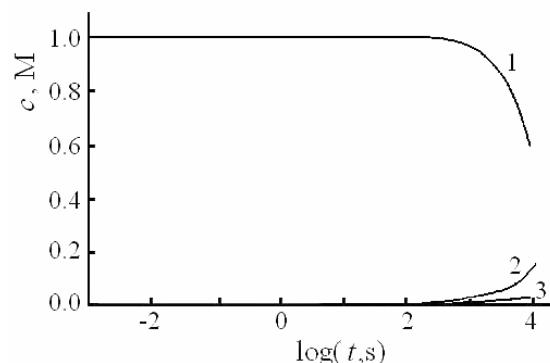


Figure 6.4. Kinetic curves for the consumption of α -methylacrolein (1) and the accumulation of α -methylacrylic (2) and α -peroxymethylacrylic (3) acids.

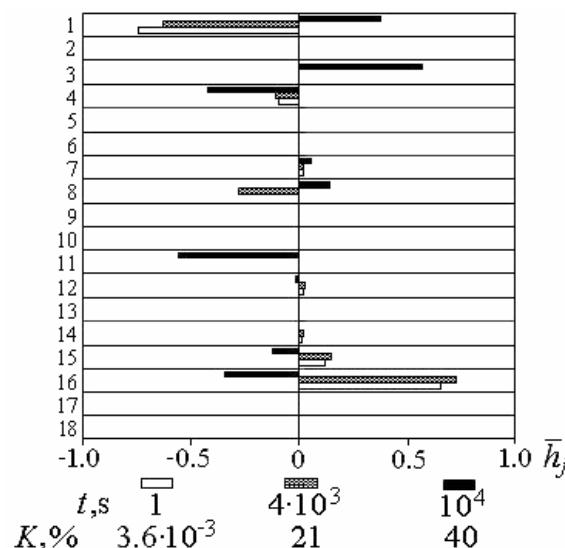


Figure 6.5. Reduced value contributions of individual steps for liquid-phase oxidation of α -methylacrolein at different reaction times and conversions. Contributions are numbered in accordance with the steps. Contributions less than 0.01 are ignored. The concentration of the inhibitor is $5 \cdot 10^{-4}$ M.

Table 6.4. Calculated selectivity (S) of α -methylacrolein oxidation* at different concentrations of the inhibitor

[In] · 10^3 M	0	0.1	40
S , mol %	25	36	77

* At 30% conversion of α -methylacrolein.

It can be seen from Figure 6.5 that at 40% conversion of the aldehyde the contributions of steps (12)-(16) become negative, and the opposite is true for steps (1) and (8) on radical generation. The most probable explanation of this fact is in the significant increase in the contribution of the chain propagation step (3). In this case increase in the concentration of RCO_3^\cdot radicals causes the selectivity to increase.

Summarizing, let us note one more remarkable fact emerging from the results of the *value* numerical analysis of the kinetic model for α -methylacrolein oxidation. The ψ_i magnitudes for the chain carriers are categorized into two classes by their importance

$$\overbrace{\psi_{\text{RCO}}(t) \approx \psi_{\text{RCO}_3}(t) \approx \psi_{\text{RCO}_2}(t) \approx \psi_{\text{HO}}(t)}^{\text{I}} > \overbrace{\psi_{\text{M}}(t) \approx \psi_{\text{MO}_2}(t)}^{\text{II}}. \quad (6.15)$$

It will be reminded that for times equal to τ_{ch} the ψ_i magnitudes for free radicals have the meaning of the constituents of chain length. The relationship (6.15) points to the “two-centered nature” of the chain reaction and on the validity of relation (6.12) derived for the condition of realizing selective inhibition.

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Chapter 7

EFFICIENT INHIBITION OF CHAIN CHEMICAL REACTIONS

In this chapter the kinetic aspects of inhibition of chemical chain reactions are discussed in detail. In the case of oxidative processes, the inhibition by small additives boils down to their antioxidant effect.

The possibilities of the *value* approach are considered to solve the problem for the non-empirical selection of an effective inhibitor, based on a determined kinetic model of the inhibited reaction. The solving of such problems is demonstrated by the liquid phase oxidation of ethylbenzene with its inhibition by phenols. The transcript of molecular design of effective antioxidant from the series of similar compounds is carried out by calculating the optimal value of the dissociation energy of the phenolic OH group (BDE_{OH}^*). The magnitude of BDE_{OH} in the optimization process acts as a control parameter, which is expressed by the rate constants of reactions involving the initial antioxidant and its intermediates.

The numerical determination of the *value* quantities as a function of time allows explaining the chemical reason of the antioxidant's effectiveness. Also the *value* method has been used to analyze the mechanisms for the liquid phase oxidation of ethylbenzene and model lipids: methyl linoleate, in the presence of antioxidants in the reaction mixture - butylated hydroxytoluene and α -tocopherol, respectively. The dominant steps responsible for the antioxidant and pro-oxidant properties of chain reaction inhibitors are identified.

These presented examples allow to conclude that the efficiency of the antioxidant is determined by its *optimal systemic behavior* with its participation in the pro-oxidant and antioxidant reactions.

Inhibition of chain reactions is an important scientific and practical problem. It is linked with the problem of reasonable selection of *efficient inhibitors*, lowering explosion hazard of the combustible materials, extending the service life of polymers, oils, monomeric compounds, food products, etc. [1-16].

The increased interest to the problem under discussion is also related to intensive investigations of the antioxidant activity of substances both of the biogenic and preparatory nature, in the peroxidation of model lipids, as well as in the autoxidation of proteins, saccharides and other constituents of a cell organism [17-28]. These investigations are aimed at revealing the mechanisms of protective action of bioactive substances in the pathogenesis of living organisms, as a result of the so-called oxidative stress. One of its manifestations

comes to the uncontrollable intensification of the chain peroxidation of lipids and other species of cells.

The term “effective inhibition” usually implies prediction of the reaction conditions and the structure of the species, which ensure the most prolonged and deep inhibition of the chain process.

In spite of the great body of kinetic information, in actual practice the empiric approach prevails in the majority of cases when selecting inhibitors. Among possible reasons to explain this fact is the labor intensiveness, and in some cases, the certain limitation of the used kinetic approaches for analyzing complicated reaction mechanisms. Nevertheless, the most operative and fundamental way to solve the problem of the efficient inhibition of chain chemical processes seems to be based on the in-depth understanding on the main points of phenomena, and not only on the intuition of an expert.

As mentioned, the solution of such a non-empirical problem requires firstly, sufficient knowledge of the mechanism of inhibitory action on the chain conversion for a certain class of substances, and secondly, on the existence of comprehensive methods for analyzing the kinetic models of the inhibited chain reactions.

Usually the effect of inhibitors consists in their direct participation or in the participation of their conversion products in certain steps of the chain process. This dictates a need to identify the role of individual steps in the efficiency of demonstration of the inhibitor properties for a complicated chemical process.

The inhibiting mechanism for chain reactions, particularly for the chain oxidation processes is studied quite thoroughly owing to their high scientific and practical importance. Without giving the history of the progress in this field we only state that the theory developed for these processes is a major contribution in chemical kinetics. To study the details of this issue the reviews and monographs [1-16] are recommended.

This chapter deals with data obtained by the application of the *value* approach to the problem of the nonempirical selection of efficient inhibitors and their use in chain reactions.

To facilitate the data presentation let us briefly describe the general kinetic laws of the inhibited chain reaction. Specific features of inhibited oxidation in the condensed phase will be discussed in detail. This is mainly conditioned by the availability of detailed data on the inhibition mechanism for the chemical reactions under consideration. In the next paragraphs they will be examined by the *value* method.

7.1. KINETIC ASPECTS OF CHAIN REACTION INHIBITION

7.1.1. The Chemical Action Mechanism of Inhibitors in Chain Reactions

By the nature of chemical effect on chain reactions the inhibitors may be subdivided into certain classes:

1. *Inhibitors breaking chains due to reactions with chain carriers.* Among such inhibitors in chain reactions occurring in the condensed phase are phenols, naphthols,

polyphenols, sulfophenols, aromatic amines, aminophenols, hydroxylamines reacting with alkyl and alkyl peroxyradicals, as well as nitroxyl radicals, quinones, iminoquinones, nitrocompounds, molecular iodine that react with carbon-centered radicals. These inhibitors usually are applied to suppress the free-radical oxidation and the polymerization processes in the condensed phase. More often completely halogen-substituted hydrocarbons (for example, freons), alcohols, nitrogen oxides, etc. are used as inhibitors in the gas phase. These compounds react with atoms and free radicals in the combustion processes.

2. *Inhibitors suppressing generation of reactive particles in chain reactions.* These inhibitors are successfully proved to impede the oxidation processes in the condensed phase. Primarily among them are the substances intensively reacting with hydroperoxides, practically without forming free radicals that may initiate the chain reactions. Usually among these are the organic compounds containing heteroatoms: sulfides, phosphites, thiophosphites, etc. It should be reminded that just the hydroperoxides serve as the basic source of free radicals, in the autoxidation of organic compounds. To this class also belong the substances (diamines, hydroxyacids, dibasic carboxylic acids, etc.) that deactivate metal ions. Metal ions, especially those of the transition metals catalyze the decomposition of peroxides into free radicals. In the reaction mixture the above-listed inhibitors form metal chelates serving as catalytic poisons, thus blocking the catalytic effect of metal ions.

To inhibit the chain chemical processes, in practice, often a mixture of inhibitors is used, including those with a different nature of action. As a rule, the composition of species is selected based on the idea that the effect of a mixture of inhibitors would exceed the effect of each individual species if they are taken in the same molar concentration. Such nonadditive action of inhibitors is known as *synergism* [5,16].

Let us discuss more detailed the inhibition mechanism of the first class.

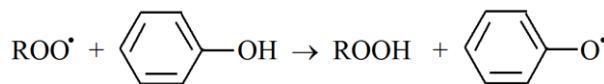
Breaking of kinetic chains at the interaction of the active reaction centers (n^\cdot) with inhibitors is interpreted as the formation of kinetically passive free radical, In^\cdot , incapable of propagating the chain conversion.

In accordance with such an idea the inhibition mechanism of chain conversion of the initial substance, A may be represented by a set of reactions:

1. $I \rightarrow n^\cdot$,
2. $n^\cdot + A \rightarrow P_1 + n^\cdot$,
3. $n^\cdot + n^\cdot \rightarrow P_2$,
4. $n^\cdot + In^\cdot \rightarrow In^\cdot + P_3$,
5. $n^\cdot + In^\cdot \rightarrow P_4$,
6. $In^\cdot + In^\cdot \rightarrow P_5$,

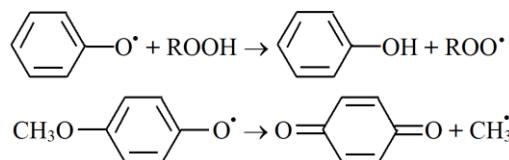
where P_i ($i = 1, 2, \dots, 5$) are the nonradical reaction products, I is the initiating agent (the initiator and/or the initial reagent).

It follows from this simplified reaction scheme that the inhibitor's radicals solely react with each other and with the chain carriers. Such a conception about the mechanism of an inhibited reaction cannot be considered as realistic. Actually the situation is more complicated so far as both the free radical In^\bullet and the inhibitor participate also in "side" reactions, which may be illustrated by the example of conversions of the phenolic compounds and their derivatives, the phenoxy radicals under the conditions of oxidation in the condensed phase. In these cases for the reaction resulting in "exchanging" the active ROO^\bullet radical by the passive phenoxy, one comes to the abstraction of a hydrogen atom from the phenol by peroxy radical.

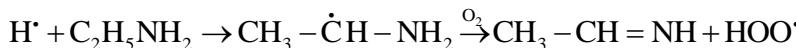


These "secondary" processes may be conditioned by the following reactions:

- *Participation of In^\bullet in the chain propagation step due to the reactions with molecular products or decomposition of In^\bullet yielding a reactive particle*, for example:



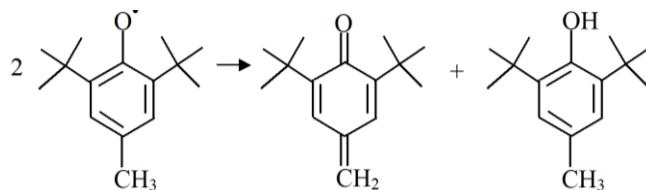
- *Quadratic reactions of In^\bullet with chain carriers giving rise to the so-called positive interactions of chains*. In this respect the illustrative example is the inhibition of hydrogen combustion (see Chapter 1) by alkylamines caused by the transformation of the reactive H^\bullet atom into the more indifferent particle, the HOO^\bullet radical



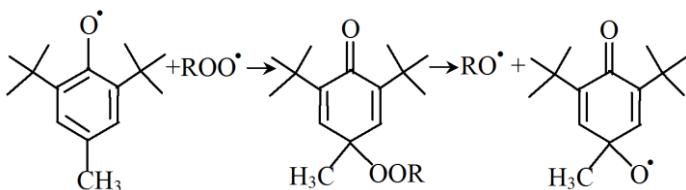
And in the quadratic interaction between the HOO^\bullet radical and the hydrogen atom two active hydroxyl radicals may be formed



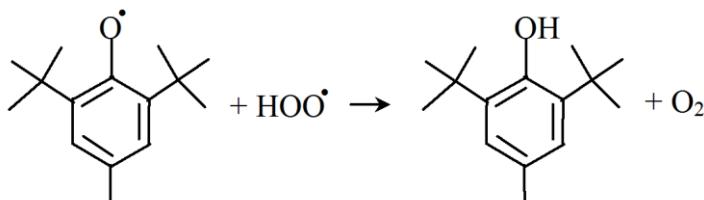
- *Reactions of In^\bullet yielding nonradical products* that influence markedly on the reaction inhibiting or promoting it. Thus, disproportionation of 2,4,6-trialkyl-substituted phenoxy radicals results in end products, the appropriate methylene quinone and the initial phenolic inhibitor, e.g.:



Recombination of 2,4,6-tri-tert-butylphenoxy radicals with peroxy ones results in quinolide peroxides, which decompose at relatively elevated temperatures forming free radicals that, in turn, promote the chain process [11].

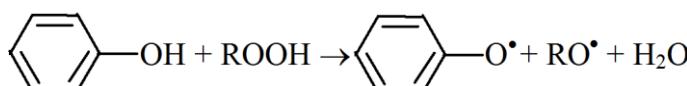


- *Regeneration of the inhibitor by the reaction of In[•] with chain carriers.* Such processes prolong considerably the effect of an inhibitor. As an illustration the reaction of the phenoxy radical with the hydroperoxyl one may be demonstrated, occurring as follows [26]:



Detailed review of examples as related to inhibitor regeneration in the liquid-phase oxidation of organic substances are found in [16].

- *Reactions of the inhibitor with initial and intermediate molecular substances.* Here initiation of the reactive centers is possible. As an illustration the interaction between phenol and hydroperoxide just formed during the reaction may be demonstrated



It may be stated as a conclusion that the problem of chain reaction inhibition may not be brought only to the reaction of the inhibitor with the chain carriers. Surely, the problem requires the comprehensive consideration of the complex inhibited reactions. A similar situation should be expected for the inhibitors that have the action of a different nature.

7.1.2. The Efficiency Parameters of Inhibitors

As efficiency of inhibitor it is implied its capability of providing the most prolonged and deep deceleration of a chain reaction. In the literature proper attention is paid to this issue [1-16], and different quantitative characteristics are provided, which define the efficiency of chain reaction inhibitors. It seems to us as positive in these approaches that a solution of the inhibitor efficiency problem is turned into the kinetic analysis of the model for inhibited reaction. Nevertheless, in most cases, the sorting out of the quantitative characteristics for inhibitor efficiency is based on occurring a definite set of reactions in the inhibited process and cannot be considered as a versatile one. In other words, their application is restricted by the degree of complexity of the used kinetic model.

One of the most attractive quantitative characteristics of inhibitor efficiency seems to be the value of a reaction's induction period. By the induction period is meant the time after which a low-intensity chemical process gives place to the reaction with growing rate or, more strictly, the time when a detectable conversion for the initial substances is achieved.

Frequently, practically total consumption of the inhibitor is observed as the induction period passes. For this reason in some researches the induction period is interpreted as the time of total consumption of the inhibitor [11].

Along with the time of reaction retardation an important characteristic of the inhibited process is the retardation depth (see Figure 7.1). E.T. Denisov [14] described the retardation depth in the presence of an inhibitor by the magnitude of chain length, v_{ln} . The smaller is the latter the greater is the extent of "freezing" the chemical transformations of the initial substance over the induction period. The efficiency of inhibitor is suggested to be defined simultaneously by two parameters, v_{ln} and the degree of "loss" of the inhibitor by side reactions, which does not cause chain breaking, ω . Such a condition is written as

$$v_{ln} \rightarrow \min, \\ \omega \leq 0.25, \quad (7.2)$$

where ω is defined as the ratio of consumption rates of the inhibitor by the side reactions and by the reactions with chain carriers. The condition (7.2) is offered instead of $\tau_{ip} \rightarrow \max$, that makes it possible to arrive at the analytical solution of the problem.

To have a more complete idea on the capability of the inhibitor to retard the chain reaction, there is a need of the additional information about the dependency of inhibitor efficiency on its concentration and temperature.

In practice preference is given to the inhibitors, which maintain their inhibiting capabilities in a wider range of temperature. In some cases it is also important up to which temperature the inhibitor does not lose its capability to "suppress" the chains. In [14] it is suggested to assess the temperature limit of inhibition as a temperature at which the inhibitor, when terminating the chains, provides a chain length that is smaller than the conventional value $v_{opt.}$

In the branching chain reactions the effect of the inhibitor in the framework of analytical approach usually is estimated by its influence on the parameter of self-acceleration φ -factor [16], which defines the propagation rate of a chain process (see Chapter 1).

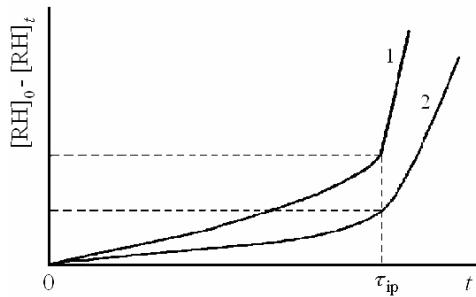


Figure 7.1. Observed depths (1,2) of process inhibition for the same induction period.

Thus, taking as a basis the conclusion that the efficiency of an inhibitor depends on a variety of factors, we want to emphasize once more the following idea. Strict comparison of the inhibitor's efficiency is feasible only for a certain concentration interval of the inhibitor and the state of the reaction system.

One more important aspect is that the efficiency of an inhibitor may be dependant on the selected regime of influencing a reaction. For instance two regimes may be selected:

- introduction of the inhibitor in the reaction system at a definite time;
- continuous (programmed) introduction of the inhibitor during the reaction.

In this situation the efficiency criterion is preferred that simultaneously takes into account both the duration and retardation depth of the reaction. Surely, using the efficiency criterion must be possible for an arbitrary regime of inhibited influencing a chain reaction.

Considering the possibility of applying the calculus of variations (see Chapter 4) for solving this problem we suggest to use as an efficiency criterion for the inhibitor the target functional (7.3) with the imposed minimality condition

$$I(t) = \Delta[RH]_t = \int_0^t r_{RH}(t) dt \rightarrow \min \quad (7.3)$$

where r_{RH} is the rate of consumption of the initial substance.

It should be reminded that applying the calculus of variations does not impose essential restrictions when selecting the initial kinetic model for the inhibited chain reaction. Note also that an assessment of the efficiency of the inhibitor's retarding action by the use of the integral target functional enables setting the problems not only for suppressing the overall reaction, but also for the inhibition of the undesirable product, the P_i accumulation. In this case the following condition must be satisfied:

$$I(t) = \Delta P_i(t) = \int_0^t r_{p_i}(t) dt \rightarrow \min, \quad (7.4)$$

where r_{p_i} is the rate of the P_i product formation.

7.1.3. Judgment on Efficiency of Inhibiting Parameters

Dependency of inhibitor efficiency on its concentration contains the characteristics of inhibitor activity. The more active is the inhibitor, the lower are the concentrations at which the decrease in chain reaction rate is observed.

For an “ideal” inhibitor, when the inhibitor and a free radical formed from it participate solely in reactions with chain carriers of a nonbranching-chain reaction, the activity according to [14,16] may be defined as follows:

$$A_{In} = (r_0 / r - r / r_0) / [In] = m k_{In} / (2 k_t r_i^0)^{1/2}, \quad (7.5)$$

where r, r_0 are the initial reaction rates with and without the inhibitor, respectively; r_i^0 is the rate of chain carrier initiation; k_t and k_{In} are the rate constants for the quadratic termination and the reaction of chain carriers with the inhibitor, respectively; $[In]$ is the initial concentration of the inhibitor; m is the stoichiometric factor of inhibition defining the number of chains being broken by one molecule of the inhibitor.

The activity characterizes the relative reaction rate decrease per unit concentration, when introducing the inhibitor into the reaction mixture.

When assuming linear mechanism for the termination of chain carriers in the absence of an inhibitor, for the activity of the inhibitor we have

$$A_{In} = (r_0 / r) / [In] = m k_{In} / k_l. \quad (7.6)$$

Here k_l denotes the rate constant for the reaction of linear termination of chain carriers in the absence of the inhibitor.

As it follows from expressions (7.5) and (7.6) the activity of an “ideal” inhibitor is defined by its capability to react with the chain carriers. In actual situations the inhibitor’s activity also depends on the intensity of a set of reactions rather than one.

In the above calculations the m value has often the meaning of a parameter, which specifies the molecular structure of the inhibitor (see [4]). For example, it is taken equal to double the number of OH-groups in the molecules of phenols. However this is not an universal interpretation because actually, as objectively mentioned in [11,30], m represents a kinetic quantity. The stoichiometric factor of inhibition being a derivative of the inhibitor’s molecular structure, is self-expressed through a set of reactions including the molecule of the inhibitor and its conversion products:

$$m = r_i^0 / r_{In} \quad (7.7)$$

where $r_{In} = -d[In] / dt$.

In branching-chain reactions the activity of an inhibitor may be characterized by its capability to shift the explosion limit. It should be noted that when stabilizing, for example, gas mixtures, in practice apart from the time of reaction retardation it is important for the inhibitor to ensure the reliable explosion safety of the mixture. Therefore, here the inhibitor activity characterizes to a certain degree its efficiency as an anti-igniting additive, as well. For this case let us confine ourselves to the “ideal” inhibition and consider the lower explosion

limit for a branching-chain reaction, similar to the one between hydrogen and oxygen (see Chapter 1). Here it is assumed the reactions of chain breaking to be conditioned by steps, including the hydrogen atom with the concentration exceeding that of other chain carriers: the oxygen atom and the hydroxyl radical. Then the inhibitor activity may be defined as

$$A_{In} = \left(\frac{1}{P_0} - \frac{1}{P_{In}} \right) / f_{In} = mk_{In} / k_t, \quad (7.8)$$

where P_{In} , P_0 denote the initial pressure for the reaction system fitting the explosion limit with and without the inhibitor, respectively; f_{In} is the molar fraction of the inhibitor in the gas mixture; and k_t is the rate constant for the linear termination of chain carriers in the absence of the inhibitor.

For the diffusion mechanism of the termination of chain carriers on the walls of a reaction vessel the rate constant for the heterogeneous termination of chain carriers is $k_t = k'_t / P$. Then the inhibitor activity is expressed by:

$$A_{In} = \left(\frac{1}{P_0^2} - \frac{1}{P_{In}^2} \right) / f_{In} = mk_{In} / k'_t. \quad (7.9)$$

When considering the second explosion limit for the gas mixture (hydrogen – oxygen) the expression for the inhibitor activity is presented in the form

$$A_{In} = \frac{P_0 - P_{In}}{f_{In}} = \frac{mk_{In}}{k_4 f_{O_2}}, \quad (7.10)$$

where f_{O_2} is the molar fraction of the oxygen in the gas mixture; k_4 is the rate constant for the homogeneous termination of chain carriers in the absence of inhibitor molecules (see Chapter 1).

By analogy with the inhibited nonbranching-chain reactions the activity of an “ideal” inhibitor in the branching-chain processes is determined through the rate constant for its reaction with chain carriers. However, here again a necessity arises to take into account the “side” reactions of the inhibitor, that is, the chemistry of the inhibitor conversions under real operating conditions. Unfortunately, the systematic researches in this direction were undertaken so far to a lesser degree than for the inhibited chain reactions in the condensed medium.

7.1.4. Nonempirical Methods for Efficient Inhibitor Selection

As stated, the most general way in the selection of an efficient inhibitor is based on the analysis of the parameters of the inhibitor’s electron structure and the detailed mechanism of

the inhibited chain reactions. This supports once again the idea that a successful suggestion of new inhibiting systems for chain processes and on improving the already known ones is highly improbable without a deep insight into the kinetic laws of inhibited reaction.

Important results are achieved in this field when studying the oxidative transformations of organic substances inhibited by phenols [4-16]. It was demonstrated with these examples that the reaction mechanisms of inhibited oxidation are nonlinear dynamical systems. In this situation they failed to obtain analytical solutions in the general case that would allow to select the key parameters of the reaction. Recommendations for the selection of inhibitor's structure and the operating conditions of materials on the basis of these parameters would be the next step.

To solve this task a kinetic "mosaic" approach (the method of "kinetic topology") was offered by E.T. Denisov (see Chapter 2). Conceptually, such an approach represents the analysis of more simple, sufficiently autonomous reaction schemes that may be solved analytically. Later, using these data one can compile the overall picture on the behaviour of an inhibited reaction. A more detailed solution of such a problem may be represented as follows [13,14]:

- the selection of key steps defining the kinetics of a complicated inhibited reaction under different conditions;
- the analysis of the autoxidation (self-accelerated or stationary) regime as a starting point for further calculations;
- the obtaining of analytical solutions for the selected simplified reaction schemes at certain acceptable assumptions;
- the finding of analytical forms for the relation between the parameters of inhibitor efficiency and the kinetic features of individual steps;
- the recommendations about the inhibitor efficiency and materials operating conditions proceeding from the obtained analytical expressions.

Within the framework of the given approach the important conclusion was made about the efficiency of an antioxidant, in particular, of the phenolic type that, for a given reaction system it may be characterized [13,14] by the dissociation energy of OH-bond in the phenol molecule (D_{OH}) and the dissociation energy of reactive CH-bond in the oxidizing substance (D_{CH}). Variation of the interval of these parameters determines the most probable occurring direction with some set of steps involving the inhibitor and the radical In^{\cdot} . Therefore it is suggested to outline beforehand the range of different and relatively simple mechanisms in the D_{CH} and D_{OH} coordinates. Such a procedure makes significantly easier the study of kinetic schemes and the revealing of the relation between the antioxidant efficiency and the energies of the OH-bond of phenol and the CH-bond of the substrate.

The above-listed stages in solving the problem on the efficient antioxidant selection in the framework of the "kinetic topology" may be represented in the form of a fundamental logic diagram (Figure 7.2).

It is precisely that such nonempirical approaches proved to be the most productive in solving the problem of the efficient inhibitor selection. And still their usage may lead to the following problems:

- not in all cases the inhibited reaction may be described by a “discrete spectrum” of sufficiently simple mechanisms; such a situation may appear when the initial conditions are varied in a wide range;
- the principles of selecting the key steps for the inhibited process occurring in an arbitrary regime require detailed investigations.

Nevertheless, it should be emphasized that this approach is valuable especially from the methodological standpoint.

Another approach has been applied by V.V. Kharitonov [29,30] when solving the task on the selection of an “operative” inhibitor. In [29,30] the analysis of mechanisms for the inhibited oxidation chain reactions comes to the numerical determination of the characteristic parameters of the reaction model (more often as a ratio of rate constants for individual steps) from the experimental kinetic data, i.e. some kind of inverse problem of chemical kinetics is solved. Then, based on these parameters an attempt was made to predict the effect of the inhibitor with a certain molecular structure. However using this undoubtedly interesting method it is not simple to achieve the required universality. The point is that these parameters themselves and their number are strongly dependant on the degree of complexity of the inhibited kinetic model and on the range of change of the initial reaction parameters (temperature, inhibitor’s concentration, etc.) as well. The use of this method is problematic if the number of steps in the kinetic model is large.

In essence, we provided a number of reasons that in addition to already known approaches stimulate the searching for new nonempirical ways in solving the problem of the effective inhibition of chain chemical reactions.

In fact, the problem of the nonempirical selection of the efficient inhibitor may be brought to the problem of optimal control, to say it is necessary to determine the reactivity parameters characterizing the inhibitor’s molecular structure that minimize the quality index of a reaction, and more often the conversion of the initial reagents or the concentration of the reaction final product(s).

For such a problem statement numerical methods may be used without principal limitations for the complexity of the kinetic model of the inhibited reaction.

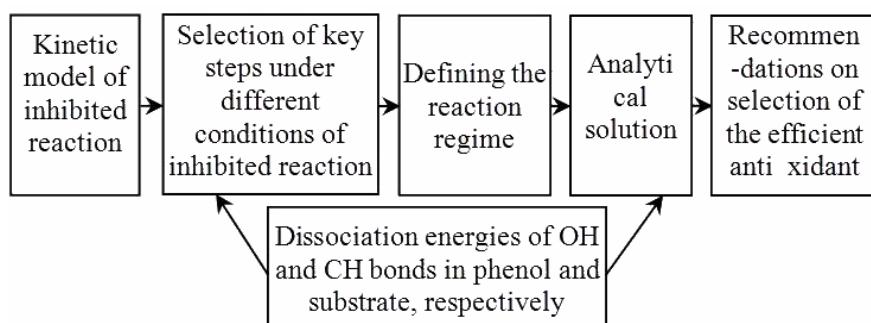


Figure 7.2. Outline of the procedures to identify an efficient antioxidant, applying the “kinetic topology” method.

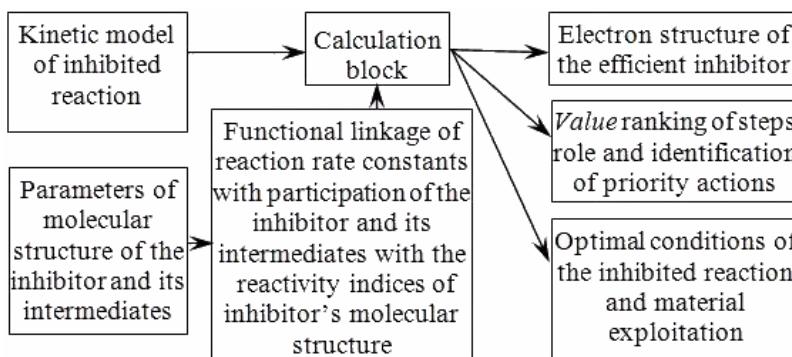


Figure 7.3. Sequence of operations at nonempirical solution of the problem on the selection of efficient inhibitor by the *value* method.

As demonstrated in Chapter 4, the *value* approach seems to be highly effective for solving such problems. It should be emphasized that this approach, in spite of revealing the molecular structure of the efficient inhibitor, enables highlighting the kinetic significance of individual steps, involving the inhibitor and its intermediates.

The mathematical apparatus of the calculus of variations forming the basis of the *value* approach for solving the controlling problems allows also to determine the optimal conditions for reaction inhibition and materials exploitation in the presence of an inhibitor.

The selection of an efficient inhibitor and optimal conditions of inhibition by the use of the *value* approach, to be discussed in detail later, can be illustrated schematically (Figure 7.3).

Attention should be focused on two kinds of information delivered to the computing block. The first is the kinetic model of an inhibited reaction in the traditional meaning, and the second are the equations linking the rate constants of reactions involving the inhibitor and its intermediates with the reactivity indices of the initial form. Conceptually, as mentioned in Chapter 4, the numerical solution of tasks shown in the right-hand member of Figure 7.3 one has to deal with the extended kinetic model, including both the initial reaction mechanism and the information about the inhibitor's reactivity and intermediates of its transformation. It should be reminded that earlier such reaction kinetic models of inhibited oxidation of organic substances were constructed in the framework of the analytical approach [14].

7.2. VALUE IDENTIFICATION OF KINETIC SIGNIFICANCE OF STEPS FOR ETHYLBENZENE OXIDATION INHIBITED BY PARA-SUBSTITUTED PHENOLS. SELECTION OF EFFICIENT ANTIOXIDANT

In this part the numerical *value* analysis is carried out [31-33] for the kinetic model on liquid-phase oxidation of ethylbenzene inhibited by *para*-substituted phenols.

We considered the kinetic model for the reaction under study to a certain extent as illustrative with an objective to demonstrate the capabilities of numerical analysis for kinetic models of the inhibited oxidation by the *value* method. It must be stated that the *value* ranking of individual steps by the degree of their kinetic participation in the liquid-phase oxidation of

ethylbenzene will allow to give a “chemical” meaning to the calculation data obtained from the inhibited reaction mechanism.

On the other hand, the *value* analysis of kinetic models for inhibited reactions enables to identify the conditions for their optimal realization. As mentioned, such a problem definition is linked with the solution of the following kinetic tasks:

- the defining of the molecular structure of the efficient inhibitor by the given kinetic model and the selected reaction conditions through the modeling;
- the revealing of the optimal initial concentration of the inhibitor.

7.2.1. Determination of the Molecular Structure of an Efficient Inhibitor and Its Effective Concentration

Information forming the basis of the kinetic trajectories of the *value* contributions for steps involving an inhibitor and its transformation products may be useful for the selection of the molecular structure of the efficient inhibitor resulting in the maximum deceleration of a reaction. However this task may be solved strictly by finding the optimum inhibitor structure and the reaction conditions [31,32].

As mentioned above, the condition from which the molecular design of an effective inhibitor is constructed, is as follows:

$$I(t) = \Delta[\text{RH}]_t = \int_0^t r_{\text{RH}}(t) dt \rightarrow \min, \quad (7.11)$$

$$r_{\text{RH}} = -d[\text{RH}]_t / dt$$

This criterion corresponds to the minimal conversion of the initial substance ($\Delta[\text{RH}]_t$) for arbitrary time t .

The procedure for finding the numerical parameters of the molecular structure for the efficient inhibitor is described in Chapter 4.

Now let us focus our attention to the task on determining the effective concentration of the inhibitor. Obviously, owing to the pro-oxidant properties of the inhibitor, a situation is possible when the maximum inhibiting effect does not coincide with the maximum initial concentration, but is within the certain range of $[\text{InH}]^{\min} \leq [\text{InH}]_0 \leq [\text{InH}]^{\max}$.

The method of determining the initial concentration of the inhibitor that results in maximum inhibition effect is based on Pontryagin’s maximum principle. For this case the kinetic equation and the appropriate Hamiltonian are written as

$$\frac{dc_i}{dt} = f_i(c_1, c_2, \dots, c_m, c_{\text{InH}}^0)$$

$$H = r_{\text{RH}} + \sum_{i=1}^m \psi_i f_i(c_1, c_2, \dots, c_m, c_{\text{InH}}^0), \quad i = 1, 2, \dots, m. \quad (7.12)$$

In this case the initial concentration of the inhibitor, $[InH]_0$, serves as the control parameter. Then, using the maximum principle described above one can derive the optimal concentration of the inhibitor, which meets the condition (7.11).

7.2.2. Kinetic Analysis of the Mechanism of Liquid-Phase Oxidation of Ethylbenzene Inhibited by *Para*-Substituted Phenols

The kinetic model of reactions. The inhibition mechanism of liquid-phase oxidation of hydrocarbons (RH) by phenolic compounds (InH) has been repeatedly discussed [1-16]. The kinetic scheme of inhibited ethylbenzene oxidation in the presence of *para*-substituted phenols, in general, includes a set of reaction steps as shown in Table 7.1. The scheme is written for oxygen pressures that are high enough to meet the condition $[R^\cdot] \ll [ROO^\cdot]$.

In Table 7.2 the correlation equations are presented for the steps (11)-(13), (16) and (17) that describe the rate constant dependency for reactions, with the participation of *para*-substituted phenol and with the corresponding phenoxy radical on the dissociation energy of OH-bond in *para*-substituted phenol.

Table 7.1. Kinetic model for liquid-phase oxidation of ethylbenzene inhibited by *para*-substituted phenols

№	Reactions	Rate constant ¹		Reference
		$t = 60^\circ\text{C}$	$t = 120^\circ\text{C}$	
1	$2RH + O_2 \rightarrow 2R^\cdot + H_2O_2$	$9.26 \cdot 10^{-13}$	$7.7 \cdot 10^{-10}$	[34,35] ²
2	$R^\cdot + O_2 \rightarrow ROO^\cdot$	$8.75 \cdot 10^8$	$1.0 \cdot 10^9$	[36]
3	$ROO^\cdot + RH \rightarrow ROOH + R^\cdot$	2.74	20	[37]
4	$RO^\cdot + RH \rightarrow ROH + R^\cdot$	$2.32 \cdot 10^6$	$5.85 \cdot 10^6$	[38] ²
5	$HO^\cdot + RH \rightarrow H_2O + R^\cdot$	10^9	10^{10}	[39]
6	$ROOH + RH \rightarrow H_2O + RO^\cdot + R^\cdot$	$1.28 \cdot 10^{-10}$	$2.72 \cdot 10^{-7}$	[40]
7	$ROOH + RH \rightarrow R(-H)O + H_2O + RH$	$3.83 \cdot 10^{-10}$	$8.16 \cdot 10^{-7}$	[41]
8	$RO^\cdot + ROOH \rightarrow ROH + ROO^\cdot$	$4.9 \cdot 10^8$	$6.43 \cdot 10^8$	[39] ²
9	$ROO^\cdot + ROO^\cdot \rightarrow 2RO^\cdot + O_2$	$5.5 \cdot 10^6$	10^7	[42-44] ²
10	$ROO^\cdot + ROO^\cdot \rightarrow ROH + R(-H)O + O_2$	10^7	$3.5 \cdot 10^7$	[42-44] ²
11	$ROO^\cdot + InH \rightarrow ROOH + In^\cdot$	$2 \cdot 10^4$	$8.5 \cdot 10^4$	[45]
12	$RO^\cdot + InH \rightarrow ROH + In^\cdot$	$2.77 \cdot 10^8$	$6.8 \cdot 10^8$	[46,47] ²
13	$ROOH + InH \rightarrow H_2O + RO^\cdot + In^\cdot$	$9.5 \cdot 10^{-8}$	$3.4 \cdot 10^{-5}$	[48]
14	$In^\cdot + ROO^\cdot \rightarrow In(-H)O + ROH$	$7 \cdot 10^8$	$7 \cdot 10^8$	[45]
15	$In^\cdot + In^\cdot \rightarrow InH + In(-H)$	$3.5 \cdot 10^8$	$3.5 \cdot 10^8$	[49]
16	$In^\cdot + RH \rightarrow InH + R^\cdot$	0.31	9.7	Calc. ²
17	$In^\cdot + ROOH \rightarrow InH + ROO^\cdot$	$5.2 \cdot 10^3$	$2.29 \cdot 10^4$	[45] ²

¹ Rate constants are presented in the units of M, s, when the reaction is inhibited by *para*-methylphenol.

² Additional comments for kinetic parameters may be found in the text.

Table 7.2. Dependence of $\log k$ ($M^{-1}s^{-1}$)* for steps with *para*-substituted phenols and appropriate phenoxyl radicals vs. dissociation energy of O-H bond of phenols, D_{OH} (kJ/mol)

t 0C	$\log k = \phi(D_{OH})$
60	$\log k_{11} = 34.24 - 0.082D_{OH}$
120	$\log k_{11} = 30.11 - 0.069D_{OH}$
60	$\log k_{12} = 17.5 - 0.025D_{OH}$
120	$\log k_{12} = 16.58 - 0.0212D_{OH}$
60	$\log k_{13} = 50.1 - 0.157D_{OH}$
120	$\log k_{13} = 44.01 - 0.133D_{OH}$
60	$\log k_{16} = -25.2 + 0.066D_{OH}$
120	$\log k_{16} = -16.30 + 0.0474D_{OH}$
60	$\log k_{17} = -22.24 + 0.072D_{OH}$
120	$\log k_{17} = -17.90 + 0.061D_{OH}$

* Index for k corresponds to the step number in Table 7.1.

Structural formula for *para*-substituted phenol is:



where R' is the substituent.

Below are presented some comments related to the kinetic parameters in Tables 7.1 and 7.2.

Reaction (1)

The value of k_1 was calculated using the Arrhenius equation $\log k = \log k^0 - E/2.303RT$, where k^0 and E are the pre-exponential factor and the activation energy of the reaction rate constant; T is the absolute temperature, R is the universal gas constant. $E_1 = -\Delta H_1^0 + 6 = 122$ kJ/mol according to [34]. Here ΔH_1^0 is the change of the standard enthalpy for reaction (1). To determine k_1 the values of E_1 and $k_1^0 = 7.51 \cdot 10^{-10} M^{-2}s^{-1}$ at 120^0C were used [34].

Reaction (4)

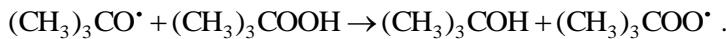
The value of k_4 was calculated using the Arrhenius equation, and for the calculation of E_4 the constant $k_4 = 1.05 \cdot 10^6 M^{-1}s^{-1}$ was used, corresponding to the reaction of *tert*-butyloxyradical with ethylbenzene at 22^0C , with the average value of $\log k_4^0 (M^{-1}s^{-1}) = 9$ [38].

Reaction (5)

It was assumed that the value of k_5 at 120^0C is close to that of the rate constant for the diffusion-controlled reaction.

Reaction (8)

The value of k_8 was calculated using the Arrhenius equation. $k_8=18$ kJ/mol is taken to be close to the activation energy of reaction (12). $\log k_8^0$ (M⁻¹s⁻¹)=11.2 was calculated using $k_8=2.5 \cdot 10^8$ M⁻¹s⁻¹ at 22 °C [38] for the reaction



Reactions (9) & (10)

The values of k_9 and k_{10} were determined from k_9+k_{10} [37] and $k_9/k_{10} = 0.28$ [43,44]. It was assumed that k_9/k_{10} does not depend on temperature and the yield of radicals formed by reaction (9) from the solvent cage is close to 1.

Reaction (11)

Equation describing the dependence of $\log k_{11}$ on D_{OH} (Table 7.2) was derived by the method of step-by-step calculation. As a basis for this served the correlation between $\log k_{11}$ and Hammett's parameters of σ *para*-substituents of the phenol at 60 °C [11,44]

$$\log k_{11} = 4.0 - 1.79\sigma . \quad (7.13)$$

Here the σ parameters of the phenol's *para*-substituents are linked with D_{OH} through the relation [11]

$$D_{OH} = 368 + 21.7\sigma . \quad (7.14)$$

Using equations (7.13) and (7.14) we obtain

$$\log k_{11} = 34.24 - 0.082D_{OH} \quad (T = 60 \text{ } ^\circ\text{C}).$$

E_{11} was calculated from the mean value of the rate constant pre-exponent for reaction (11): $\log k_{11}^0$ (M⁻¹s⁻¹) = 7.2 [38]

$$E_{11} = 2.303(\log k_{11}^0 - \log k_{11})RT = 0.52D_{OH} - 172.4 .$$

Then, using the Arrhenius equation the dependence of $\log k_{11}$ on D_{OH} at $t = 120$ °C was found.

Reaction (12)

The dependence of $\log k_{12}$ on D_{OH} was derived from the equation

$$\log k_{12} = 11 - (0.16D_{OH} - 42)/2.303RT \quad (7.15)$$

Equation (7.15) was obtained from the data of rate constants for the reaction of *tert*-butyloxyl radical with *para*-substituted phenols [46,47]. It was also assumed that the pre-exponent of the rate constant for reaction (12) is weakly dependent on the molecular structure of the *ortho*-nonsubstituted phenol. The value of k_{12} was calculated from (7.20) for $D_{\text{OH}}=364.4 \text{ kJ/mol}$, corresponding to the dissociation energy of the OH-bond in *para*-methylphenol [11].

Reaction (13)

The dependence of $\log k_{13}$ on D_{OH} was derived from the appropriate equation in [50]

$$\log k_{13} = 10.26 - (D_{\text{OH}} - 254)/2.303RT.$$

Reaction (16)

The dependence of $\log k_{16}$ on D_{OH} was derived from the correlating equation in [50] using the data of [45]

$$\log k_{16} = -1.7 - 0.056\Delta H_{16}^0, (T = 60^{\circ}\text{C}). \quad (7.16)$$

Taking into account that the dissociation energy of the α -C-H bond in the ethylbenzene equals to 343 kJ/mol [51] we have

$$\Delta H_{16}^0 = 343 - D_{\text{OH}}. \quad (7.17)$$

From (7.16) and (7.17) the dependence of $\log k_{16}$ on D_{OH} at 60°C was found.

The equation for $\log k_{16}$ at 120°C was derived by the method of step-by-step calculation applied earlier for reaction (11). At that the value $\log k_{16}^0 (\text{M}^{-1}\text{s}^{-1})=9.2$ [38] was used.

Reaction (17)

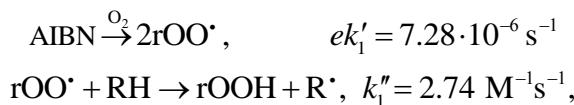
The dependence of $\log k_{17}$ on D_{OH} was derived from the correlating equation [51]

$$\log k_{17} = 4.1 + 1.56\sigma, (T = 60^{\circ}\text{C}). \quad (7.18)$$

The calculation scheme for 120°C was similar to that applied to step (11) taking into consideration that $\log k_{17}^0 (\text{M}^{-1}\text{s}^{-1})=7.2$.

Numerical description of experiments. As we have already mentioned, the selected kinetic model for liquid-phase oxidation of ethylbenzene inhibited by *para*-substituted phenols was studied in detail and describes the available experimental data with good accuracy. Nevertheless, we have conducted special experiments [31] (see the conditions in the captions to Figures 7.4 and 7.5) to confirm additionally the adequacy of the selected kinetic model.

To calculate the experimental data at 60°C performed under the regime of ethylbenzene oxidation initiated by AIBN, step (1) in Table 7.1 was replaced by the following reactions:



where k'_1 is the rate constant for the AIBN decomposition [37], e is the yield of radicals from the solvent cage taken equal to 0.7, k''_1 is the rate constant for the hydrogen atom abstraction by the cyanoisopropylperoxy radical taken as equal to the value of k_3 .

As follows from Figures 7.4 and 7.5 the calculated kinetic curves on the accumulation of ethylbenzene hydroperoxide describe experimental results with reasonable accuracy for the ethylbenzene oxidation inhibited by the *para*-methylphenol and without the inhibition at 60°C and 120°C.

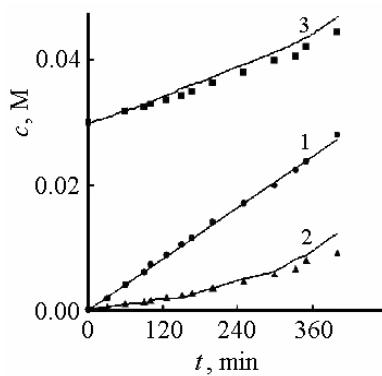


Figure 7.4. Kinetic curves of the ethylbenzene hydroperoxide accumulation for ethylbenzene oxidation initiated by AIBN without (1) and with (2) $6 \cdot 10^{-4}$ M *para*-methylphenol; (3) at simultaneous presence of $6 \cdot 10^{-4}$ M *para*-methylphenol and 0.03 M ethylbenzene hydroperoxide, $[\text{AIBN}]_0 = 4 \cdot 10^{-3}$ M, $T = 60$ °C (points – experimental; lines – calculation).

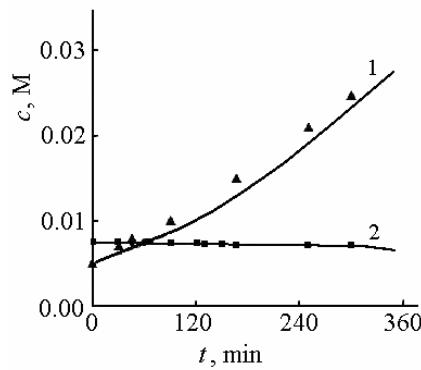


Figure 7.5. Kinetic curves of the ethylbenzene hydroperoxide accumulation (1) and *para*-methylphenol consumption (2) for liquid-phase oxidation of ethylbenzene at 120 °C. Initial concentrations of ethylbenzene hydroperoxide and *para*-methylphenol were $5 \cdot 10^{-3}$ M and $7.5 \cdot 10^{-3}$ M, respectively (points – experimental; lines – calculation).

Kinetic trajectories of the value contributions of individual steps. Computing was carried out for the following initial conditions: $[RH]_0=7.82$ and 7.35 M , at $T=60$ and $120\text{ }^{\circ}\text{C}$, respectively, $[ROOH]_0=10^{-5}\text{ M}$, $[O_2]=10^{-2}\text{ M}=\text{const}$. From kinetic trajectories of the *value* contributions of individual steps (Figure 7.6a,b) in the induction period, the following specific features of ethylbenzene oxidation inhibited by *para*-substituted phenols may be marked out.

a) **Kinetic modes of inhibited reaction.** According to the results illustrated in Figure 7.6a the liquid-phase oxidation of ethylbenzene inhibited by *para*-methylphenol at $60\text{ }^{\circ}\text{C}$ conventionally passes through three time stages:

1. $t < 3 \cdot 10^2\text{ s}$ corresponds to the time interval of establishing the quasistationary mode for *para*-methylphenoxy radicals. For this reason reaction (15) on disproportionation of phenoxy radicals occurs partially. This time interval is also characterized by the high positive contribution of step (11), the reaction of peroxy radicals with the inhibitor, and the significant negative contribution of reaction (16) between the *para*-methylphenoxy radicals and the ethylbenzene.
2. The interval $3 \cdot 10^2\text{ s} < t < 5 \cdot 10^6\text{ s}$ corresponds to the non-autoinitiated reaction. Within this interval the main step of free radical generation is presented by reaction (1). Inhibition of ethylbenzene oxidation is basically conditioned by step (15), the disproportionation of phenoxy radicals.
3. The interval $5 \cdot 10^6\text{ s} < t < 5 \cdot 10^7\text{ s}$ corresponds to the autoinitiation mode within the induction period of ethylbenzene oxidation. Generation of free radicals takes place by steps (6) and (13) with the participation of hydroperoxide formed during the interaction. Within this time interval the contribution of step (14), the reaction between phenoxy and peroxy radicals, in the inhibition of the oxidation process becomes considerable.

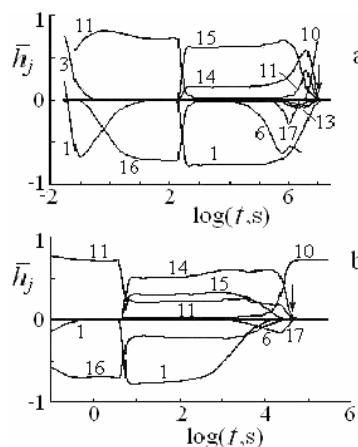


Figure 7.6. Kinetic trajectories of reduced *value* contributions of steps over the induction period for liquid-phase oxidation of ethylbenzene inhibited by *para*-methylphenol at $60\text{ }^{\circ}\text{C}$ (a) and $120\text{ }^{\circ}\text{C}$ (b). Initial concentrations of *para*-methylphenol and ethylbenzene hydroperoxide were 10^{-3} M and 10^{-5} M , respectively (curves are numbered in accordance with step numbers in Table 7.1, the arrow points out the end of the induction period).

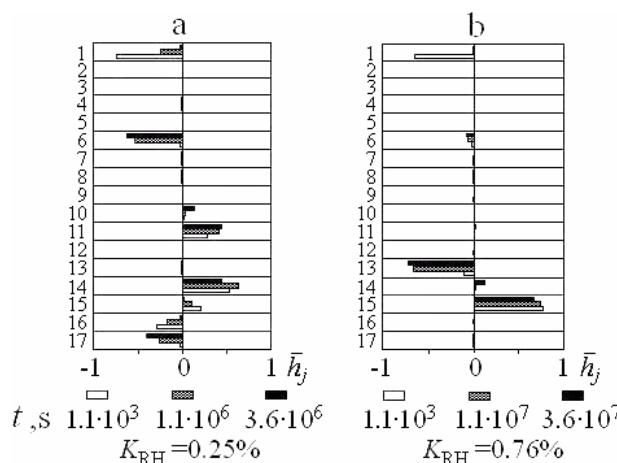


Figure 7.7. Reduced *value* contributions of individual steps (N denotes step number) over the induction period for liquid-phase inhibited oxidation of ethylbenzene at different reaction times at 60 °C. Contributions less than 0.01 are ignored. Initial concentration of the *para*-methylphenol was 10^{-4} M (a) and 0.1 M (b).

It should be pointed out that just after the induction period, a drastic change in the contribution of individual steps (h_j) takes place including the increase in the contribution of step (10), the chain breaking due to the interaction between the peroxy radicals, and the decrease in the contribution of steps (14) and (15), the chain breaking with the participation of the phenoxy radicals.

The characteristic time intervals mentioned above, selected from the kinetic trajectories of the *value* contributions, “correlate” with the kinetics of phenoxy radical accumulation. It follows from Figure 7.8 that completion of the first time interval (t_1) corresponds to establishing the quasi-stationary mode of *para*-methylphenoxy radical accumulation. Over the time interval $t_2 - t_3$ the growth in the concentration of phenoxy radicals is observed as a consequence of increasing the role of degenerate chain branching steps. Finally, mounting to the maximum value, the concentration of phenoxy radicals decreases because of inhibitor consumption.

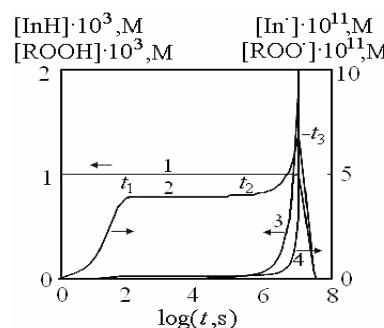


Figure 7.8. Calculated kinetic curves of *para*-methylphenol consumption (1), accumulation of *para*-methylphenoxy radical (2), hydroperoxide of ethylbenzene (3) and peroxy radical (4) for the liquid-phase inhibited oxidation of ethylbenzene at 60 °C. Initial concentration of ethylbenzene hydroperoxide was 10^{-5} M.

A similar picture for time profiles of the *value* contributions is observed at the higher temperature, 120 $^{\circ}\text{C}$ (see Figure 7.6b). For the mentioned concentration of *para*-methylphenoxy (10 ^{-3}M) the following time intervals may be marked out:

$$1) \ t < 5\text{ s}, 2) \ 5\text{ s} < t < 4 \cdot 10^2\text{ s}, 3) \ 4 \cdot 10^2\text{ s} < t < 5 \cdot 10^4\text{ s}.$$

However, at 120 $^{\circ}\text{C}$, in contrast to the oxidation at 60 $^{\circ}\text{C}$, under the conditions of identical initial concentration of the inhibitor, the *value* contribution of step (14), the cross-reaction of the phenoxy radical with the peroxy one, prevails over the contribution of step (15), the disproportionation of the phenoxy radicals for a longer period. This is concerned with the higher concentration of peroxy radicals at 120 $^{\circ}\text{C}$ resulting in the fractional increase in kinetic significance of step (14), occurring with the participation of free radicals.

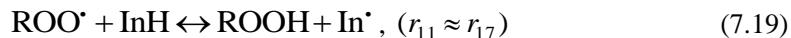
Changing the initial concentration of *para*-methylphenol causes no change in the overall picture of the time profiles of the *value* contributions (see, for example, Figure 7.7). However, growth in the inhibitor concentration results in the considerable increase in the contribution of step (13), which is responsible for the generation of free radicals with the participation of the inhibitor. Just this circumstance confines the possibility of using high concentrations of *para*-substituted phenols for the inhibition of the chain oxidation processes. This issue will be discussed later once again. Simultaneously, over the induction period the contribution of step (15), the interaction of phenoxy radicals with each other resulting in the chain breaking, becomes increasingly noticeable.

- b) Ranking the steps by the value contribution.** Kinetic trajectories for step contributions enable also to identify the most influencing steps in terms of the inhibiting effect on the process. A major part of the induction period at ethylbenzene oxidation fits to time regimes 2 and 3 (see above). Over this time the highest negative impact is caused by steps (1),(6),(13), which result in the free radical generation. On the contrary, the steps of mutual interaction of peroxy and phenoxy radicals, those of (10),(14),(15) influence favorably on the oxidation reaction inhibition.

The contributions of steps (16) and (17) are relatively small, even though they occur at higher rates, as compared to the rates of the free radical generation by the steps (1),(6) and (13). Most likely, this is concerned with the fact that in these steps, in parallel with the transformation of the relatively passive phenoxy radical into the more active free radicals, R^{\bullet} and ROO^{\bullet} , also a molecule of the inhibitor is formed. Here, of no small importance is the role of the inessential difference between the reactivity of free radicals In^{\bullet} and ROO^{\bullet} in the chain propagation steps that will be discussed below.

Minor contributions of steps (8),(9) and (12) throughout the inhibition process ($\bar{h}_j < 10^{-5}$) enabled to consider them as redundant ones. Excluding these steps from the kinetic scheme practically shows no influence on the kinetics of the concentration change (discrepancy is less than 5%) for the chemical species RH , InH , ROOH , In^{\bullet} , ROO^{\bullet} over the reaction induction period.

c) **Kinetic pattern of inhibited oxidation.** In our opinion worthy of notice is the following attractive fact. The results of computing have shown that the reaction of ethylbenzene oxidation came out from the induction period with incomplete consumption of the inhibitor (where the conversion of ethylbenzene is about 2%). The effect is observed in all cases at 120^0C , and predominantly for the relatively high values of D_{OH} (see Table 7.3) at 60^0C . This is associated with establishing the quasi-equilibrium of reactions (11) and (17)



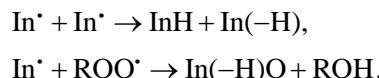
that results in the reproduction of the inhibitor's molecule by a reverse reaction.

Such equilibrium becomes as more “stable” over the induction period of the reaction with increasing D_{OH} value, as a result of the increase in the rate constant of the reverse reaction (17). In this case, the inhibition effect decreases because of the equilibrium displacement in the direction of formation of a more reactive (in the chain propagation stage) peroxy radical.

In fact, *para*-substituted phenols with dissociation energy of phenolic O-H bond exceeding 375 kJ/mol do not inhibit ethylbenzene oxidation at 60^0C .

The inhibiting effect of the phenol under quasi-equilibrium conditions may be reduced to the following:

1. The reaction of the peroxy radical with the inhibitor's molecule (step 11) yields phenoxy radicals, In^\cdot , that participate in the disproportionation steps (14) and (15)



2. The fraction of peroxy radicals, reacting more effectively with the initial hydrocarbon, decreases in the reaction system.

Because of an intensive reaction between the phenoxy radical and the hydroperoxide ($r_{17} > r_6 + r_{13}$), the breaking of chains takes place due to the disproportionation of the phenoxy radical by steps (14) and (15) and is not limited by the reaction of the peroxy radical with the inhibitor (step 11).

It is particularly remarkable that at small concentrations of the inhibitor (at less than 10^{-4} M), the reaction rate of the peroxy radical with the phenol (step 11) decreases drastically and becomes the rate-limiting stage in the inhibition of ethylbenzene oxidation. As a consequence, the positive contribution of this step becomes substantial (see Figure 7.8). At the same time, when a sufficient amount of hydroperoxide is accumulated in the reaction system, the negative contribution of the reaction between the phenoxy radical and the hydroperoxide (step 17) increases as if it is “counteracting” step (11). Such a picture is common for the reaction at 60^0C and 120^0C .

Table 7.3. Conversion (K_{InH}) of the inhibitor depending on the dissociation energy of O-H bond (D_{OH}) in the molecule of *para*-methylphenol at coming out the inhibited reaction from the induction period*

K_{InH} , %	99	47	30	25	7	2	0.1	0.1
D_{OH} , kJ/mol	355	360	362	365	370	375	380	382.5
$\tau_{ip} \cdot 10^{-3}$, hour	58.3	41.7	33	22.2	8.3	2.8	1.1	1.1

* $T = 60^{\circ}\text{C}$, $[\text{InH}]_0 = 0.01 \text{ M}$, $[\text{ROOH}]_0 = 10^{-5} \text{ M}$.

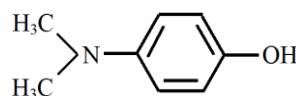
The above discussed experimental data and those obtained in [53] are indicative of the above described equilibrium (7.19). It follows from Figure 7.4 that introducing the hydroperoxide into the reaction mixture in the initiation mode (at $T = 60^{\circ}\text{C}$) leads to the increase of the oxidation rate. Note that under these conditions the rate of radical decomposition of the hydroperoxide is negligible as compared to that of initiation by AIBN. The reason for the rate increase due to introducing the hydroperoxide into the reaction mixture is in the displacement of equilibrium (7.19) to the left, causing growth in the concentration of the peroxy radical, which is reactive in the chain propagation.

The experiment performed at 120°C (see Figure 7.5) also points to the existence of such an equilibrium. The reaction comes out from the induction period at the expense of the hydroperoxide accumulation, responsible for the autoinitiation of the oxidation at an incomplete conversion of the inhibitor. This is evidence of the inhibitor regeneration by reaction (17).

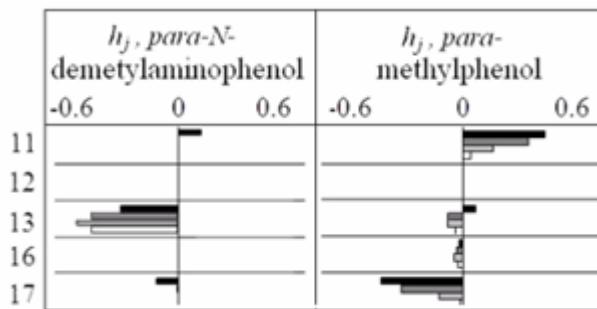
Numerical determination of molecular structure of the efficient inhibitor based on the reaction kinetic model. The molecular structure of *para*-substituted phenol having a maximum inhibiting ability in the ethylbenzene oxidation was determined by the method described above. The dissociation energy of the O-H bond in the phenols (D_{OH}) served as the characteristic reactivity indices for the molecular structure of the inhibitor. By this value it has been possible to describe the reactivity of appropriate phenoxy radicals (see Table 7.2)

$$355 \leq D_{OH} \leq 382.5 \text{ kJ/mol.}$$

Using the maximum principle and considering D_{OH} as a *control parameter* the optimum values of D_{OH}^{\bullet} conforming to an efficient inhibitor were determined. These values were derived for different initial concentrations of the inhibitor. Within a broad concentration range ($10^{-4} \div 10^{-1} \text{ M}$) D_{OH}^{\bullet} took the minimum possible value (355 kJ/mol) both at 60 and 120°C , to which corresponds the following molecular structure of the *para*-substituted phenol:



It was defined using the value $\sigma = -0.6$ [54] for the *para*-substituent parameter. According to equation (7.18), to this σ corresponds the value of $D_{OH}^{\bullet} = 355 \text{ kJ/mol}$ for the efficient inhibitor.



\bar{h}_j is the reduced *value* contribution for the j -th step.

Figure 7.9. Reduced *value* contributions depending on D_{OH} in liquid-phase oxidation of ethylbenzene inhibited by efficient antioxidants: *para*-*N*-dimethylaminophenol ($\text{R}'\equiv\text{N}(\text{CH}_3)_2$, $D_{\text{OH}}=355 \text{ kJ/mol}$) and *para*-methylphenol ($\text{R}'\equiv\text{CH}_3$, $D_{\text{OH}}=365 \text{ kJ/mol}$) at $T = 60^\circ\text{C}$. Initial concentrations of the antioxidant and the hydroperoxide of ethylbenzene were 10^{-3} and 10^{-5} M , respectively. Conversion of ethylbenzene

■ ■ ■ □
 $(\%.10^4)$: -18, -10, -3.2, -0.47.

Value contributions of steps (11-13,16,17) involving inhibitor and phenoxy radical with the rate constant “sensitive” to the reactivity indices D_{OH} contain useful information. According to data shown in Figure 7.9, for the “nonoptimal” inhibitor, *para*-methylphenol, step (11) and its reverse reaction (17) have the most significant contributions. And in the case of the optimum inhibitor, *para*-*N*-dimethylaminophenol, *value* contributions of steps (11) and (17) for the equilibrium (7.19) decrease substantially. Hence it follows that the efficient inhibitor that has the minimum magnitude of D_{OH} , mainly provides for the maximum displacement of equilibrium (7.19) to the right: from the chain carrier (peroxy radical) to the formation of the phenoxy radical.

Determination of the optimal initial concentration of the inhibitor. For *para*-substituted phenols the optimal initial concentration was found, $[\text{InH}]_0^{\text{opt}}$, which is the concentration where for higher values the efficiency of inhibition for the reaction of ethylbenzene autoxidation falls off. This result is in line with the data obtained for the *in vivo* and the *in vitro* autoxidation (peroxidation) of lipids [25] inhibited by the bioantioxidant α -tocopherol. As shown, when increasing the concentration its inhibiting effect falls down considerably because of the appearance of pro-oxidant properties. A similar picture was observed for the antioxidant stabilization of the carbochain polymers [12]. It is noteworthy that the optimal concentration of the *para*-substituted phenol increases with increasing in D_{OH} (Figure 7.10), which is associated with the important initiation role of the chain reaction, with participation of the inhibitor in step (13).

As it follows from the results demonstrated in Figure 7.7, just a substantial increase in the contribution of step (13) with raising the temperature explains the observed decrease in $[\text{InH}]_0^{\text{opt}}$ (more than an order) at 120°C , as compared to that of 60°C (see Figure 7.10).

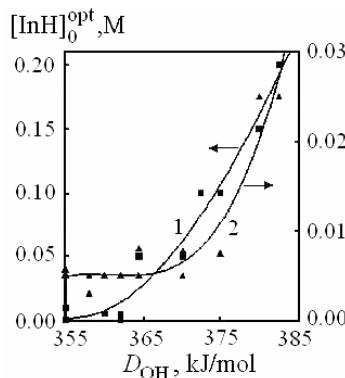
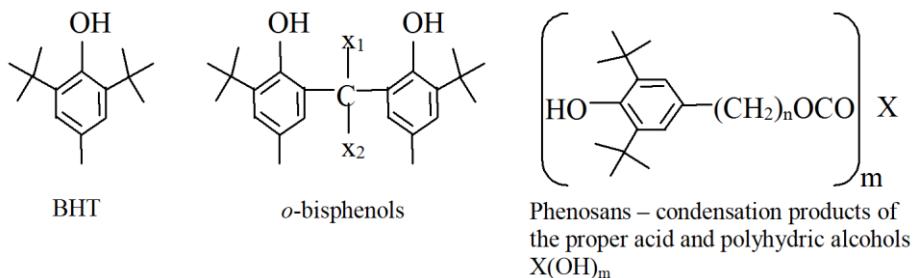


Figure 7.10. Optimum initial concentration of *para*-substituted phenol, $[InH]_0^{opt}$ vs. bond dissociation energy D_{OH}^{\bullet} , resulting in maximum inhibition of ethylbenzene oxidation at $T = 60\text{ }^{\circ}\text{C}$ (1) and $T = 120\text{ }^{\circ}\text{C}$ (2).

7.3. VALUE IDENTIFICATION OF STEPS' KINETIC SIGNIFICANCES IN THE MECHANISM OF ETHYLBENZENE OXIDATION INHIBITED BY BUTYLATED HYDROXYTOLUENE

Ortho-alkylsubstituted phenol: 2,6-di-*tert*-butyl-4-methylphenol (butylated hydroxytoluene, BHT) and its structural analogues are efficient antioxidants. They are widely used for the stabilization of polymers and technical oils [1-16]. Being almost nontoxic, BHT is applied as antioxidant in food products. At the same time BHT and its structural analogues serve as an active basis for several widely used medicines of bioantioxidant nature, such as dibunolum and probucol [55]. Molecular structures for some *ortho*-alkylsubstituted phenolic antioxidants are shown below:

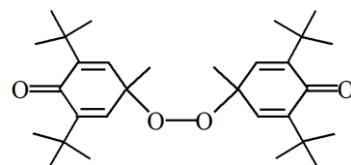


Analysis of kinetic models for chain reactions on the oxidation of organic substrates in the presence of BHT enables the mechanism with its participation to be compared with that of the sterically unhindered phenols discussed in the preceding section. Besides, it allows the obtaining of further insight into the reason of the inhibitor efficiency and the receiving of useful information to predict new structures of the efficient antioxidants.

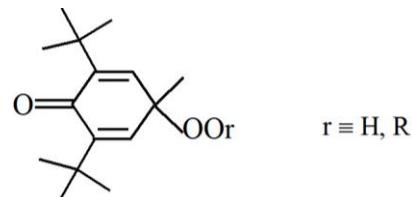
7.3.1. Kinetic Analysis of the Mechanism for Liquid-Phase Oxidation of Ethylbenzene Inhibited by BHT

Kinetic model of the reaction. The mechanism of inhibiting the action of BHT in oxidation reactions of organic substances was thoroughly investigated in [1-16]. The kinetic model for the ethylbenzene oxidation inhibited by BHT [33] is demonstrated in Table 7.4. Based on already established ideas about the inhibition mechanism of BHT we proceeded from the maximum possible extended kinetic model, including in the scheme the steps (6),(7),(15),(16),(18),(25), (26), (31) with the hydroperoxyl radical and the steps (8),(12),(33),(34) with hydrogen peroxide. The scheme is written for the case of ethylbenzene oxidation at sufficiently high oxygen pressures when the condition $[R\cdot] \ll [ROO']$ is met.

QP₁ is symmetric *para*, *para*-quinolide peroxide, for example:



QP₂ is asymmetric quinolide *para*-peroxide or hydroperoxide, for example:



Below we present some comments on Table 7.4.

Reactions (1) – (5), (9) – (11), (13), (14)

The rate constants of these steps correspond to the model of ethylbenzene oxidation inhibited by *para*-methylphenol (see the preceding section).

Reaction (6)

The rate constant for reaction (6) was taken to be approximately three times greater than that of reaction (3).

Reaction (18)

The rate constant for reaction (18) was taken to be approximately three times greater than that of reaction (17).

Table 7.4. Kinetic model for the reaction of liquid-phase oxidation of ethylbenzene inhibited by BHT

№	Reactions	Rate constants ¹			Reference
		T=37 °C	T=60 °C	T=120 °C	
1	$2RH + O_2 \rightarrow 2R^\bullet + H_2O_2$	$3.52 \cdot 10^{-14}$	$9.26 \cdot 10^{-13}$	$7.7 \cdot 10^{-10}$	[34,35]
2	$R^\bullet + O_2 \rightarrow ROO^\bullet$	$8.75 \cdot 10^8$	$8.75 \cdot 10^8$	$1 \cdot 10^9$	[36]
3	$ROO^\bullet + RH \rightarrow ROOH + R^\bullet$	0.98	2.74	39	[37]
4	$RO^\bullet + RH \rightarrow ROH + R^\bullet$	$1.48 \cdot 10^6$	$2.32 \cdot 10^6$	$5.85 \cdot 10^6$	[38]
5	$HO^\bullet + RH \rightarrow H_2O + R^\bullet$	10^9	10^9	10^9	[39]
6	$HOO^\bullet + RH \rightarrow H_2O_2 + R^\bullet$	2.94	7.62	60	[38] ²
7	$HOO^\bullet + ROOH \rightarrow H_2O_2 + ROO^\bullet$	$6.35 \cdot 10^2$	$1.05 \cdot 10^3$	$3 \cdot 10^3$	[38]
8	$ROO^\bullet + H_2O_2 \rightarrow ROOH + HOO^\bullet$	$1.05 \cdot 10^2$	$1.68 \cdot 10^2$	$4.4 \cdot 10^2$	[56]
9	$RO^\bullet + ROOH \rightarrow ROH + ROO^\bullet$	$1.47 \cdot 10^8$	$4.9 \cdot 10^8$	$6.43 \cdot 10^8$	[38]
10	$ROOH + RH \rightarrow RO^\bullet + H_2O + R^\bullet$	$3.47 \cdot 10^{-12}$	$1.28 \cdot 10^{-10}$	$2.72 \cdot 10^{-7}$	[40]
11	$ROOH + RH \rightarrow R(-H)O + H_2O + RH$	$1.04 \cdot 10^{-11}$	$3.83 \cdot 10^{-10}$	$4.08 \cdot 10^{-7}$	[41]
12	$H_2O_2 + RH \rightarrow R^\bullet + H_2O + HO^\bullet$	$6.76 \cdot 10^{-11}$	$1.06 \cdot 10^{-10}$	$1.62 \cdot 10^{-7}$	[57]
13	$ROO^\bullet + ROO^\bullet \rightarrow 2RO^\bullet + O_2$	$3.5 \cdot 10^6$	$5.5 \cdot 10^6$	10^7	[42-44]
14	$ROO^\bullet + ROO^\bullet \rightarrow ROH + R(-H) + O_2$	10^7	10^7	$3.5 \cdot 10^7$	[42-44]
15	$ROO^\bullet + HOO^\bullet \rightarrow ROOH + O_2$	$3 \cdot 10^8$	$3 \cdot 10^8$	$3 \cdot 10^8$	[43]
16	$ROO^\bullet + HOO^\bullet \rightarrow R(-H)O + H_2O + O_2$	$1 \cdot 10^8$	$1 \cdot 10^8$	$1 \cdot 10^8$	[43]
17	$ROO^\bullet + InH \rightarrow ROOH + In^\bullet$	$1.3 \cdot 10^4$	$2.04 \cdot 10^4$	$6.94 \cdot 10^4$	[58]
18	$HOO^\bullet + InH \rightarrow H_2O_2 + In^\bullet$	$3.9 \cdot 10^4$	$6.12 \cdot 10^4$	$2.08 \cdot 10^5$	[38] ²
19	$RO^\bullet + InH \rightarrow ROH + In^\bullet$	$2.16 \cdot 10^6$	$4.54 \cdot 10^6$	$2.1 \cdot 10^7$	[59]
20	$ROOH + InH \rightarrow In^\bullet + RO^\bullet + H_2O$	$9.25 \cdot 10^{-9}$	$1.75 \cdot 10^{-7}$	$6.7 \cdot 10^{-5}$	[60] ²
21	$InH + O_2 \rightarrow In^\bullet + HOO^\bullet$	$1.53 \cdot 10^{-13}$	$5.8 \cdot 10^{-12}$	$8.77 \cdot 10^{-9}$	[61]
22	$In^\bullet + In^\bullet \rightarrow InH + In(-H)$	$6.42 \cdot 10^3$	$1,1 \cdot 10^4$	$3.3 \cdot 10^4$	[61]
23	$In^\bullet + In^\bullet + O_2 \rightarrow QP_1$	$4.9 \cdot 10^3$	$4.9 \cdot 10^3$	$4.9 \cdot 10^3$	[62]
24	$In^\bullet + ROO^\bullet \rightarrow QP_2$	$3 \cdot 10^8$	$3 \cdot 10^8$	$3 \cdot 10^8$	[11,52]
25	$In^\bullet + HOO^\bullet \rightarrow InH + O_2$	$1.5 \cdot 10^8$	$1.5 \cdot 10^8$	$1.5 \cdot 10^8$	[38] ²
26	$In^\bullet + HOO^\bullet \rightarrow QP_2$	$6.5 \cdot 10^8$	$6.5 \cdot 10^8$	$6.5 \cdot 10^8$	[64] ²
27	$In^\bullet + ROOH \rightarrow InH + ROO^\bullet$	0.3	1	15.23	[52]
28	$In^\bullet + RH \rightarrow InH + R^\bullet$	$3 \cdot 10^{-7}$	$1.91 \cdot 10^{-6}$	$6.96 \cdot 10^{-5}$	[13,64] ²
29	$QP_2 \rightarrow 2 RO^\bullet$	$4.94 \cdot 10^{-10}$	$2.09 \cdot 10^{-8}$	$4.13 \cdot 10^{-5}$	[11]
30	$QP_1 \rightarrow 2 RO^\bullet$	$6.3 \cdot 10^{-9}$	$2 \cdot 10^{-7}$	$4.5 \cdot 10^{-4}$	[11]
31	$HOO^\bullet + HOO^\bullet \rightarrow H_2O_2 + O_2$	$3.5 \cdot 10^8$	$3.5 \cdot 10^8$	$3.5 \cdot 10^8$	[65]
32	$ROOH + InH \rightarrow P + H_2O$	$2.5 \cdot 10^{-8}$	$4.73 \cdot 10^{-7}$	$1.8 \cdot 10^{-4}$	[60] ²
33	$In^\bullet + H_2O_2 \rightarrow InH + HOO^\bullet$	0.3	1	15.23	[38] ²
34	$InH + H_2O_2 \rightarrow In^\bullet + HO^\bullet + H_2O$	$9.25 \cdot 10^{-9}$	$1.75 \cdot 10^{-7}$	$6.7 \cdot 10^{-5}$	- ²

¹ Rate constants are presented in the units of M, s.² Additional comments for kinetic parameters may be found in the text.

Reactions (20) and (32)

The rate constants for reactions (20) and (32) were derived from the Arrhenius equation, taking into account that $k_{20}/(k_{20}+k_{32}) = 0.27$ [60] and $k_{20}+k_{32} = 3 \cdot 10^{-4} \text{ M}^{-1}\text{s}^{-1}$ at 120^0C . It was supposed that activation energies are equal to that of the similar reaction with the participation of *para*-methylphenol, which is 109.5 kJ/mol [11].

Reactions (25) and (26)

The rate constant for reaction (25) was taken to be two times smaller than that of reaction (15), and the rate constant for reaction (26) to be approximately two times greater than that of reaction (24).

Reaction (27)

The values for the rate constants at 37 and 120^0C were determined using the Arrhenius equation. As a basis for this served the correlation between $\log k_{27}$ and the Hammett parameters of *σ* *para*-substituents of *ortho-tert*-butylsubstituted phenols [52]:

$$\log k_{27} = 0.28 + 2.18\sigma.$$

The value of σ for the methyl group equals to -0.17 . Then, the value of E_{27} , may be calculated using $\log k_{27}^0(\text{M}^1\text{s}^{-1}) = 7.2$ [38]

$$E_{27} = 2.303(\log k_{27}^0 - \log k_{27})/RT,$$

Where $\log k_{27}^0$ and E_{27} are the pre-exponent and the activation energy of reaction (27), respectively.

Reaction (28)

The rate constant for reaction (28) was calculated using the correlating equation [13] with the correction that the molecule of ethylbenzene takes part in the reaction. Thus,

$$\log k_{28} = 43.08 + 0.11D_{\text{OH}}, \text{ at } T = 60^0\text{C}.$$

where D_{OH} is the dissociation energy of the O-H bond being 339 kJ/mol in the case of BHT [11, 13]. Then the rate constants at 37 and 120^0C were derived using the Arrhenius equation. Here, it was accepted that $\log k_{28}^0 = 5$ [63].

Reaction (29)

It was supposed that *para*-quinolide hydroperoxide decomposes yielding free radicals with the same rate constants as *para*, *para*-quinolide peroxide have.

Reactions (33) and (34)

The rate constants for reactions (33) and (34) were accepted to be equal to those for reactions (27) [52] and (20) [60], respectively.

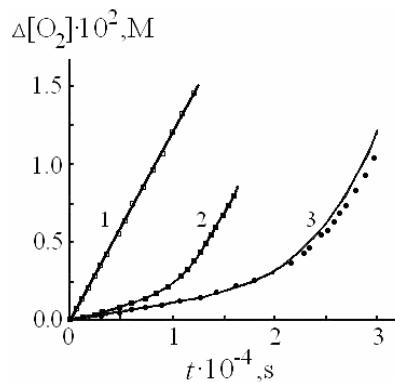


Figure 7.11. Kinetic curves of oxygen absorption at ethylbenzene oxidation initiated by AIBN in the absence (1) and presence (2 and 3) of BHT. $[BHT]_0 = 3.3 \cdot 10^{-4}$ M (2) and $6.4 \cdot 10^{-4}$ M (3), respectively, $T = 60^\circ\text{C}$, $[AIBN]_0 = 4 \cdot 10^{-3}$ M (points – experimental; curves – calculation).

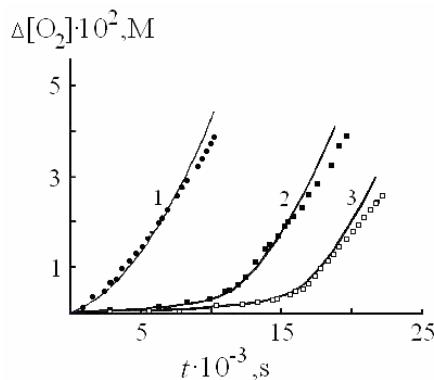


Figure 7.12. Kinetic curves of oxygen absorption for ethylbenzene oxidation in the absence (1) and presence (2 and 3) of BHT. $[BHT]_0 = 6.5 \cdot 10^{-5}$ M (2) and $1 \cdot 10^{-4}$ M (3), respectively, $T = 120^\circ\text{C}$. The initial concentration of ethylbenzene hydroperoxide was $1 \cdot 10^{-3}$ M (points – experimental; curves – calculation).

Experimental results and their numerical description. It follows from results shown in Figures 7.11 and 7.12 that calculated kinetic curves for oxygen absorption describe with reasonable accuracy the experimental data for the oxidation of ethylbenzene at 60°C and 120°C , inhibited by butylated hydroxytoluene and without it.

When modeling the oxidation of ethylbenzene initiated by AIBN at 60°C step (1) is replaced by the AIBN decomposition (see Table 7.4) ultimately resulting in two radicals with rate constants $7.28 \cdot 10^{-6}$ s⁻¹ (taking into consideration that the parameter $e = 0.7$, characterizing the yield of radicals from the solvent cage).

Kinetic trajectories of value contributions of individual steps. Numerical calculation of *value* contributions of steps was performed at the following initial conditions: $[RH]_0 = 8.02$, 7.83, and 7.35 M at $T = 37$, 60 and 120°C , respectively; $[ROOH]_0 = 10^{-5}$ M, $[O_2] = 10^{-2}$ M = const. The calculated kinetic trajectories of *value* contributions over the induction period

of the inhibited oxidation of ethylbenzene (see Figures 7.13-7.16) enable to highlight the following features of the reaction:

- When comparing the data of these figures one can clearly see the symbiosis between the accumulation of phenoxy radicals and the dynamics of quadratic steps with their participation, steps (22) and (24). Here, the growth of negative influence of steps (27), (29), (10) may be tracked at the detectable consumption of the inhibitor, when the hydroperoxide of ethylbenzene and the quinolide peroxides are accumulated in the system.
- The main negative effect is contributed by the steps of autoinitiation (steps 10, 29), due to the radical decomposition of hydroperoxide and the non-symmetric quinolide peroxide (step 29), as well as by the step of “exchange” of phenoxy radicals for the peroxy ones (27). It should be noted that the role of these steps in ethylbenzene oxidation inhibited by BHT is exclusively negative at all the studied temperatures, including the one at 37°C.
- Contribution of the step of radical decomposition of quinolide peroxide increases substantially at elevated temperatures. So, in some cases the contribution of this step at 120°C may exceed that of the step of the radical decomposition of the ethylbenzene hydroperoxide.
- The most essential positive role play the reactions of chain carriers, peroxy radicals, with the inhibitor’s molecule (step 17) and reactions of the quadratic termination of phenoxy radicals (steps 22 and 24). At relatively low BHT concentrations ($<10^{-3}$ M) the contribution of reaction (24) is higher than that of reaction (22). This effect is particularly pronounced when hydroperoxide and quinolodic peroxides are accumulated in the system. Thus, the rate of radical generation increases, correspondingly the concentration of peroxy radicals, which results in the “cross” termination of phenoxy radicals by step (24). At the higher contents ($>10^{-3}$ M) of the inhibitor in the reaction system the contribution of reaction (22) between the phenoxy radicals prevails over the reaction (24) (see Figure 7.16) because of the comparative upgrowth in the content of the phenoxy radicals against the peroxy ones (see Table 7.5).
- Increasing in the inhibitor’s initial concentration leads to the essential raising of the negative contribution of the chain autoinitiation step (20) that involves the inhibitor’s molecule.
- The following regularity was observed: increase in the positive role of step (17) is accompanied with the same tendency for the reverse reaction (27) of the phenoxy radical with hydroperoxide.

Let us consider the following specific feature of the ethylbenzene oxidation inhibited by BHT, consisting in the substantial role of the chain propagation reaction, as a result of the interaction between the phenoxy radicals and the hydroperoxide molecule (step 27). Examination of step rates enabled to conclude that in some cases the rates of steps (17) and (27) are commensurable, that is, the reaction of peroxy radicals with BHT is close to equilibrium under such conditions. To all appearance, when using *ortho*-substituted phenol (BHT) unlike the sterically unhindered phenols considered in the previous section, the role of step (27) must be minor due to its relatively small rate constant. However, one must reckon

with the fact that in the case of inhibiting the oxidation of ethylbenzene by BHT, the relative concentration of phenoxyl radicals per unit concentration of the peroxy ones is considerably higher (see Table 7.5), by reason of which the rate of step (27) prevails over that of the reverse step (17).

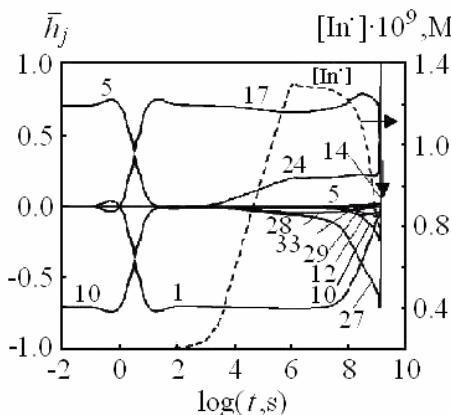


Figure 7.13. Kinetic trajectories of reduced *value* contributions of steps and accumulation of phenoxyl radicals (In^\bullet) over the induction period for liquid-phase oxidation of ethylbenzene inhibited by BHT at $37\text{ }^\circ\text{C}$. Initial concentrations of BHT and ethylbenzene hydroperoxide were 10^{-4} M and 10^{-5} M , respectively (curves are numbered in accordance with the step numbers in Table 7.4, the vertical arrow points out the end of the induction period).

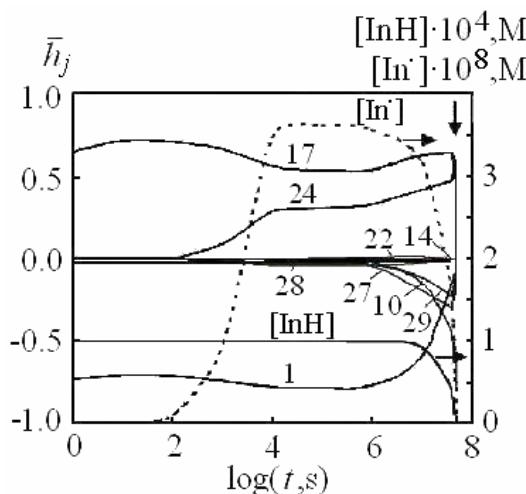


Figure 7.14. Kinetic trajectories of reduced *value* contributions of steps, the accumulation of phenoxyl radicals (In^\bullet) and the consumption of inhibitor over the induction period for liquid-phase oxidation of ethylbenzene inhibited by BHT at $60\text{ }^\circ\text{C}$. The initial concentrations of BHT and ethylbenzene hydroperoxide were 10^{-4} M and 10^{-5} M , respectively (curves are numbered in accordance with the step numbers in Table 7.4, the vertical arrow points out the end of the induction period).

And finally, the point of view set forth by V.A. Roginsky [11] seems to be quite convincing, stating that the molecular structure of BHT is close to that of the optimal inhibitor from this class of substances. Indeed, phenoxy radicals formed from BHT most intensively react with each other, especially at the high inhibitor concentrations. At the same time, as this reaction occurs intensively, it causes a fall in the possibility of initiating agents (quinolide peroxides) formation by reactions between the phenoxy and the peroxy radicals (steps 24 and 25). Of no small importance is also the relatively low activity of the phenoxy radicals in the reaction with hydroperoxide, playing a crucial role in the inhibition of the oxidation process.

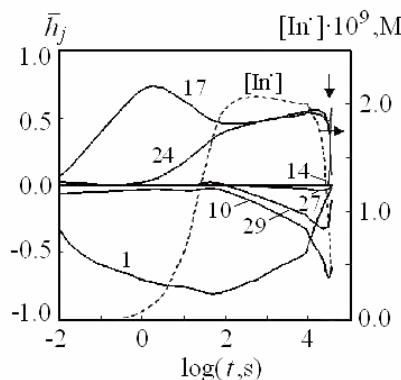


Figure 7.15. Kinetic trajectories of reduced *value* contributions of steps and accumulation of phenoxy radicals (In^\bullet) over the induction period for liquid-phase oxidation of ethylbenzene inhibited by BHT at $120\text{ }^\circ\text{C}$. The initial concentrations of BHT and ethylbenzene hydroperoxide were 10^{-4} M and 10^{-5} M , respectively (curves are numbered in accordance with the step numbers in Table 7.4, the vertical arrow points out the end of the induction period).

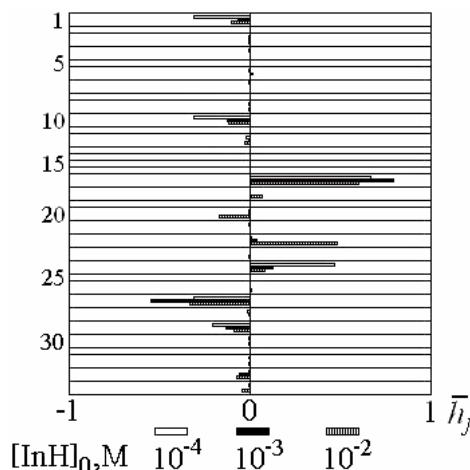


Figure 7.16. Reduced *value* contributions of individual steps over the induction period for liquid-phase oxidation of ethylbenzene inhibited by BHT at different initial concentrations: 10^{-4} M , 10^{-3} M and 10^{-2} M , $T=60\text{ }^\circ\text{C}$. The initial concentration of ethylbenzene hydroperoxide was 10^{-5} M . Step contributions are numbered according to the steps. Conversion of BHT makes up 7-10%.

Changes in the molecular structure of the inhibitor leading to the decrease in the dissociation energy of the O-H bond, consequently an increase in the rate constant and a decrease in the degree of reversibility for the reaction of peroxy radicals with the inhibitor, apparently will not give the desired result. The matter is that in this case the role of the autoinitiation step (20) involving the inhibitor's molecule is considerably enhanced at concentrations $10^{-3} \div 10^{-1}$ M that are found in practical use.

7.3.2. Reduction of Mechanism for Oxidation of Ethylbenzene Inhibited by BHT. Prognostic Capability of the Kinetic Model

Value ranking of steps enables also to solve the problem of the excessive mechanism reduction for the ethylbenzene oxidation inhibited by BHT, and, as a result, a base (minimal) reaction mechanism is identified.

As a criterion of step unimportance a condition is chosen according to which the exclusion of "low-valuable" steps from the reaction kinetic model should result in changes in the current concentrations of RH, InH, In^\bullet , ROOH, ROO^\bullet at no more than 3.5%. Monitoring was performed for two reaction times corresponding to 10-20% and 60-70% conversions of BHT. Preliminary ranking of the steps by their *value* contributions was carried out in the time range from 10^{-7} s to τ_{ip} . Within the mentioned time interval ($\bar{h}_j < 10^{-5}$) steps with small *value* contributions were selected as the "candidates" for excluding from the kinetic model. The dominant and most unimportant steps were defined unambiguously. Selection of the steps for the base model was performed among the steps with average magnitudes of *value* contributions (from two to four steps) *via* their sequential exclusion from the reaction scheme, following the above-mentioned criterion for unimportant steps.

The identified base mechanisms for ethylbenzene oxidation inhibited by BHT under different initial conditions, including the experimental conditions, are given in Table 7.6. Additionally the extended base reaction mechanism is presented, which is common for all the conditions of the inhibited oxidation reaction.

From data presented in Table 7.6 it is easy to note that increasing the initial concentration of BHT causes some extending in the appropriate base mechanism. So, with increasing the BHT concentration the steps (6),(18),(25),(26) with the participation of the hydroperoxy radical, as well as the steps (33) and (34) - the reactions of the hydrogen peroxide with BHT and the phenoxy radical, and the autoinitiation step (20) with the participation of BHT molecule are involved in the base mechanism.

Table 7.5. Calculated concentration ratio $[\text{In}^\bullet]/[\text{ROO}^\bullet]$ for liquid-phase oxidation of ethylbenzene inhibited by BHT and *para*-methylphenol under different initial conditions of reactions*

$T, ^\circ\text{C}$	$[\text{In}^\bullet]/[\text{ROO}^\bullet]$					
	$[\text{BHT}]_0, \text{M}$			$[\text{para-methylphenol}]_0, \text{M}$		
	10^{-4}	10^{-3}	10^{-2}	10^{-4}	10^{-3}	10^{-2}
60	$3.8 \cdot 10^3$	$2.4 \cdot 10^4$	$4.5 \cdot 10^5$	0.05	0.094	0.94
120	10^2	$1.8 \cdot 10^3$	$2 \cdot 10^4$	0.05	0.26	1.15

* The conversion of antioxidants (BHT and *para*-methylphenol) is 9-10%.

Table 7.6. Base mechanisms for liquid-phase oxidation of ethylbenzene inhibited by BHT at different initial conditions including those of numerical (see captions of Figures 7.13-7.16) and experimental (see captions to Figures 7.11 and 7.12) investigations

Reduction of the reaction mechanism for oxidation of ethylbenzene inhibited by BHT

□ denotes the unimportant steps of the model under the considered conditions;

□ denotes the unimportant steps of the model for the selected changing interval of initial conditions (US);

■ denotes steps in the basic model (BM):

GBM denotes the general base kinetic model;

* Experimental initial conditions.

What does the reliability of prognosis depend on? It is very important that the base mechanism describing the experimental data to be correlated with the base mechanism by which the behavior of the inhibited reaction for new initial conditions is predicted. Coincidence of these two base reaction mechanisms is the very criterion of the correctness of the prognosis. As stated in Chapter 3 this task is of current importance when the behavior of the reaction is predicted for the most prolonged reaction times, as compared to the reasonable duration of the experimental kinetic study. Just such a problem is faced when predicting the inhibitor's action in a practical application, for example, at a high inhibitor content in the initial mixture.

A satisfactory coincidence for the dominant steps is observed at 120 $^{\circ}\text{C}$. Such a coincidence in the base mechanisms may be somewhat considered as an indicator of good prognostic capability of the kinetic model.

An essential difference was observed between the base mechanisms under the experimental conditions of the initiated oxidation and those determined by the prognosis at 60 $^{\circ}\text{C}$ for the oxidation reaction inhibited by BHT.

Thus, the *value analysis* enables to structure "chemically" the prognosis. As a result new experiments can be planned that are described by constructing the kinetic models, to provide a more reliable prediction of the behavior of an inhibited reaction. For example, it can be recommended to study the reactions under the conditions of lower initiation rates so that the pro-oxidant role of the inhibitor is unsuppressed. Or, alternatively, to plan experiments with the additions of hydrogen peroxide, hydroperoxide, quinolide peroxides that would "reveal" a wider set of steps in the base mechanism required to perform an adequate prognosis. However, as it follows from the results obtained at 120 $^{\circ}\text{C}$ and the reliable kinetic information about the initial reaction mechanism, the analysis of the inhibited reaction is evidently valid also for 60 $^{\circ}\text{C}$ and 37 $^{\circ}\text{C}$.

7.4. METHYL LINOLEATE PEROXIDATION INHIBITED BY α -TOCOPHEROL

α -Tocopherol (Figure 7.17) is recognized as the most important antioxidant with respect to protection against oxidative peroxidation of membrane lipids of the living organisms' cells [66-70]. The reaction of methyl linoleate oxidation by molecular oxygen in the presence of α -tocopherol is widely used as a model one for peroxidation of natural lipids. For this reaction a kinetic model including 53 individual steps, 22 initial and intermediate chemical species was developed [68].

This kinetic model describes experimental kinetic data at 40 and 50 $^{\circ}\text{C}$ with sufficient accuracy in a wide range of the initial concentrations of α -tocopherol (TH) and lipohydroperoxide (LOOH).

The *value analysis* enabled to classify rigorously reactions with participation of TH and intermediates of its transformation both the antioxidant and pro-oxidant temper depending on the *value* sign.

Using the *value* excess criterion for individual steps we succeeded in revelation of the base mechanism including 36 steps that ensured deviation no more than 6% between the calculated data and primary calculation for the initial kinetic model (53 individual steps).

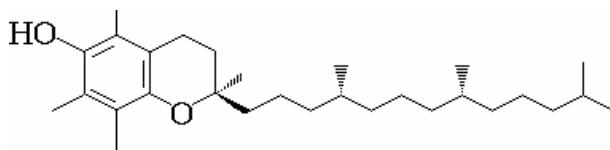
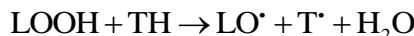


Figure 7.17. Chemical structure of α -tocopherol (5,7,8-trimethyl tocol).

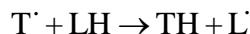
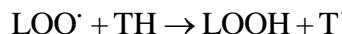
By application of *value* analysis the nature of decreasing in antioxidant efficiency of TH, i.e. the rate increase during the induction period of the reaction and reducing of the induction period with the growth of α -tocopherol concentration above $5 \cdot 10^{-3}$ M was identified.

Two main reasons of this phenomenon were disclosed by the *value* analysis of the reaction kinetic model.

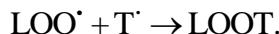
1. Intensification of the autoinitiation reaction with increase in the initial concentration of TH interacting with lipohydroperoxide



2. Chain peroxidation by means of α -tocopherol. Tocopheroxyl radical, T^\cdot , formed by interaction between TH and peroxy radical, LOO^\cdot , takes an active part in chain propagation: cleavage of the hydrogen atom from the oxidizable substance (LH)



As the initial concentration of TH increases, so does the relative content of T^\cdot radicals, $[\text{T}^\cdot]/[\text{LOO}^\cdot]$, and accordingly increases the chain length with participation of T^\cdot . Thus, the rate of chain propagation with participation of T^\cdot exceeds that of chain breaking in the cross-reaction with peroxy radical:



CONCLUSION

In the current section the capabilities of the *value* analysis of kinetic models for the inhibited oxidation of organic substances were demonstrated. A key aspect in such an approach is the identification of the kinetic significance of steps with the participation of an inhibitor and the products of its transformation. Based on these data one can recommend the ways to raise the degree and depth of the chemical reaction inhibition. For the given kinetic model a numerical method is offered to determine the molecular structure of the efficient inhibitor. Let us remind the calculation scheme consisting of three stages:

1. Representing the rate constants for the steps involving the inhibitor and the intermediate products of its transformation through the dependencies on the parameters of the inhibitor's molecular structure.
2. Determining the values for molecular parameters of the inhibitor resulting in the maximum inhibition of a chemical reaction based on calculus of variations, where the reactivity indices of the inhibitor are presented as control variables.
3. Identifying the molecular structure of the efficient inhibitor on the basis of the calculated molecular characteristics.

As an example a model of the liquid-phase oxidation of the ethylbenzene in the presence of inhibitors, the *para*-substituted phenols and the butylated hydroxytoluene, was selected. The identified dynamics of the *value* contribution of steps in the reaction mechanism is complicated. The dominant steps for the different time intervals of the inhibited reaction were determined. The inhibition mechanism of the ethylbenzene oxidation by sterically unhindered phenols is conditioned by establishing equilibrium (7.24) in the reaction of the chain carrier, the peroxy radical, with the inhibitor's molecule (within sufficiently wide interval of the inhibitor's initial concentration), followed by the reaction radical's quadratic termination with the participation of the phenoxy radical. The *value* analysis has established that the efficient inhibitor with low dissociation energy of the phenolic O-H bond promotes shifting the mentioned equilibrium from the chain carrier to the direction of the phenoxy radical formation.

For *para*-substituted phenols an optimal initial concentration of the inhibitor, $[InH]_0^{\text{opt}}$ exists, where a decrease in the inhibition effect takes place. As shown, this is associated with the fact that at relatively high inhibitor concentrations the contribution of the autoinitiation step with the participation of the inhibitor becomes important. Calculations have shown that the magnitudes $[InH]_0^{\text{opt}}$ decrease with the lowering of the dissociation energy of the phenolic O-H bond and the elevating temperature.

For the reaction of the ethylbenzene oxidation inhibited by BHT the negative contribution of steps with the participation of the quinolide peroxides formed just by the transformations of *ortho*-substituted phenols is characteristic. In the case of applying BHT, as a rule, a substantial negative contribution is introduced by the reaction of the phenoxy radical with the hydroperoxide, the reverse reaction of the peroxy radical with BHT. At first sight this result seems to be unexpected, so far as the rate constant of the reaction between the *ortho*-substituted phenoxy radical and the hydroperoxide is significantly smaller than that of the similar reaction with the *ortho*-nonsubstituted phenoxy radicals. As numerical experiments have shown, the reason is that unlike the *ortho*-nonsubstituted phenols, in the case of the *ortho*-substituted phenols the reaction occurs under a kinetic mode with relatively high predominance in the concentration of the phenoxy radicals over the peroxy ones. In other words, in the case of BHT the role of the reaction between the phenoxy radical and the hydroperoxide increases at the expense of the concentration factor.

The point of view seems reasonable that BHT and its structural analogues from the class of inhibitors under discussion are close to the molecular structure of the efficient phenolic antioxidant. At low inhibitor concentrations the *value* analysis points to the availability of the potential to raise the antioxidant efficiency by variations in the molecular structure of the

inhibitor, which would result in weakening the phenolic O-H bond. Thus, the reactivity of the antioxidant increases with respect to the peroxy radical and the degree of reversibility for the reaction between them decreases. However, at the same time a negative role of the autoinitiation reaction involving the inhibitor's molecule increases considerably at its high concentrations ($10^{-3}\div 10^{-1}$ M), as found in practice.

Our offered method for the assessment of the prognosis reliability level, for the inhibiting action of substances beyond the experimental conditions, through the reaction kinetic models, seems promising. The following strategy is applied. Experiments are planned to make a better similarity between the two base kinetic models identified by the *value* method, the first of which is defined under experimental conditions, and the second - under the prognostic conditions of a reaction.

Using as an example the kinetic model of peroxidation for a model lipid, methyl linoleate, in the presence of a bioantioxidant, α -tocopherol, the capability of *value* analysis for revealing individual chemical steps responsible for one or another manifestation of the chemical action of antioxidants was demonstrated.

In closing it should be noted that principal conclusion resulting from numerical *value* investigations of the inhibited chian reactions is that *efficiency of inhibitors, antioxidants is determined by their optimum action in a reaction system*. Just this serves as a basis for the effective application of the numerical *value* method in solving similar problems.

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Chapter 8

VALUE APPROACH IN THE SOLUTION OF PROBLEMS OF NONLINEAR CHEMICAL DYNAMICS AND SYNERGETICS

The self-organization processes are inherent in biological systems. Self-organization is also typical for the chemical reactions occurring far from equilibrium. In these reactions, the process of self-organization manifests itself in the form of concentration oscillations of the intermediate reaction species. The Belousov-Zhabotinsky (B-Zh) reaction has been studied widely as an example of an oscillating reaction. B-Zh and other reactions such as oscillating clock chemical reactions proceed in different: oscillating, stationary and chaotic modes. At that, the transition from one reaction mode to the other is critical, i.e. it occurs with small changes in initial conditions and of reaction parameters. The *value* method of numerical identification and investigation of critical reaction conditions, elaborated for the branching chain reactions, was also used for the oscillating chemical reaction systems. The generality of solving the problem to reveal the critical states is conditioned by the fact that in both cases a manifestation of criticality requires branching stages of active intermediates (as reverse positive feedback) and their inhibition (as reverse negative feedback). The revelation of critical states of the skeletal “Oregonator” model for the B-Zh reaction by the *value* method allowed to construct the phase diagram of the reaction. In the phase diagram the regions of different modes of reaction processing, depending on the initial concentration of species are strictly delineated. Thus, with the help of *value* quantities the kinetic significances of individual steps for stationary and oscillating modes of a reaction are revealed.

8.1. SELF-ORGANIZATION OF SYSTEMS. DYNAMIC REGIMES OF SYSTEMS BEHAVIOR

The ability of self-organization, that is, the spontaneous formation and evolution of complex time- and space-ordered structures [1-7] is one of the striking manifestations of biological systems. This is realizable from the thermodynamic standpoint, as biological systems are not closed but they exchange energy with the ambient environment. It is precisely the flow of energy (basically solar) that makes it possible to have the formation of ordered complex structures, followed by the dissipation of energy and entropy. That is why I. Prigogine [1] defines such structures as dissipative. Such a phenomenon is studied by a

comparatively new discipline – synergetics. The term “synergetics” (from the Greek συνεργεία - joint, concerted action) was introduced by the German physicist H. Haken [8] in the early 1970s. The problems of synergetics are studied quantitatively using the approaches of nonlinear dynamics, which are based on nonlinear mathematical models for the self-organizing systems [9-14]. It should be reminded that classical mathematical physics deals with linear equations.

In addition to biological processes, the self-organization of systems is typical for those of a diverse nature, such as the dynamics of financial markets, population development, electronics, etc. Self-organization is also typical for the chemical reactions occurring far from the equilibrium due to time-coordinated (coherent) interactions between the species of a complex chemical system [10-17]. Coherent behavior of a chemical reaction may be expressed in the form of concentration oscillations for the intermediate and end-products of the reaction, as well as for other output parameters (photoluminescence, electrochemical current, potential, etc.). Such reactions are very informative models for the complicated self-organizing processes. The reaction of Belousov-Zhabotinsky [18-20] is the most completely studied coherent reaction. Using this reaction as an example, the mathematical methods for studying the process of time-synchronization of the reactions were widely tested [19-39]. For this reason we referred just to this example to demonstrate the potential of the *value* approach in the investigation of chemical oscillation systems. Oscillating systems, including the chemical oscillators, exhibit three fundamental types of dynamic behavior: stationarity, quasi-periodicity with oscillations of clock-like precision, and randomness. The chaotic behavior of a system is generally defined as oscillations with aperiodic amplitude [9-16,40,41]. For more clarity let us address the basic concepts of the coherent dynamic systems. The behavior of such systems is described by the diagrams of the *phase space*, usually in the coordinates including the parameters of system species. The oscillating chemical reaction forms a closed trajectory in phase space, a *limit cycle*, repeated over time, as shown in Figure 8.1. The cycles may be *stable* and *unstable*. Stable cycles with the strictly periodic oscillatory behavior of a reaction are defined as *attractors*, as all other close trajectories tend to the attractor's trajectory.

Unstable cycle is the result of a *strange (chaotic) attractor*. It represents a set of cycles of complicated geometry, which “attract” the nearby passing trajectories. To predict the behavior of trajectories for chaotic systems over a long period is impossible, because of the very high sensitivity to the initial conditions of a reaction. In experiments the initial conditions are usually given with limited accuracy. It is also very difficult to reproduce numerically the trajectory for the chaotic regime of a reaction due to the approximate nature of numerical methods.

Changeover of the mentioned three reaction regimes is itself critical and exhibits high sensitivity to initial conditions, often representing initial concentrations of reagents and temperature [10-16, 40-46]. Predicting the dynamic behavior of systems is an urgent task, and this is closely related to the problem of forecasting the behavior of chaotic systems, which is often disrupted sharply from a strictly self-organized process mode. Among these are the biological and biochemical oscillating processes, taking place at the myocardium contraction, in nerve cells, mitochondria, etc. [5-7].

Mathematical simulation is a modern efficient tool in the investigation of coherent processes that enables to establish the nature of the dynamic behavior of a reaction system. It follows from the above discussion that elaboration of new computer-aided calculation

methods identifying the models' behavior in the nonlinear dynamic systems, is a pressing problem. Certainly, it seems important to use the possibilities of the numerical *value* method to study the complex multistep dynamic systems. Firstly, the *value* method allows identifying the significance of the steps and thereby the cause-and-effect relations, the “driving forces” of the complex reaction systems. Moreover, this approach may reveal the role of parameters in the behavior of target-oriented systems, expressed as functionals. This allows us to suppose that in the framework of the *value* approach we will succeed to predict the conditions of one or another evolution state of a system with time. First results of such investigations are presented in this Chapter.

8.2. BELOUSOV-ZHABOTINSKY OSCILLATORY REACTION AND ITS MATHEMATICAL MODELS

8.2.1. Main Steps of the Belousov-Zhabotinsky Reaction

In this section we will focus our attention on the chemical mechanism of the Belousov-Zhabotinsky (B-Zh) reaction. As mentioned above, the B-Zh reaction is one of the most extensively studied among the oscillating chemical reactions [15-47]. The classical B-Zh oscillating reaction system presents the oxidation of malonic acid (MA) by bromate ion (potassium bromate) in an acid medium (sulfuric acid), catalyzed by the single-electron $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox couple. The oxidized form of the catalyst, the Ce^{4+} ion, is yellow colored, and the reduced one, Ce^{3+} , is colorless. The periodicity of the B-Zh reaction is detected as a periodic yellow coloring of the solution.

In 1972, Field, Kor  s and Noyes (FKN) [21] suggested a mechanism for the B-Zh reaction involving kinetic data for individual steps and thermodynamic characteristics. The high magnitude of the Gibbs free energy for the B-Zh reaction promotes its proceeding, which results in the formation of bromomalonic acid, CO_2 and other products.

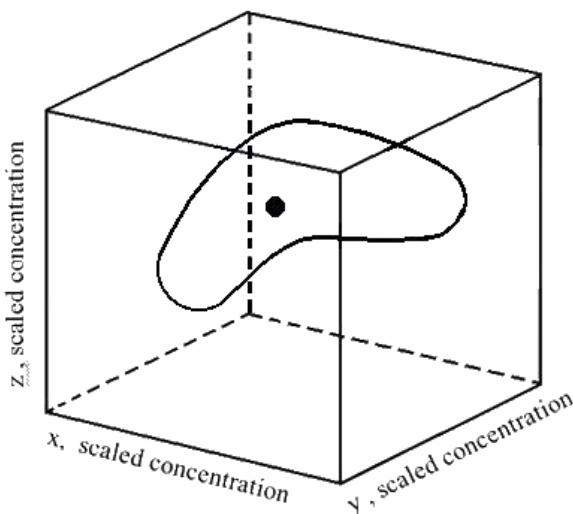
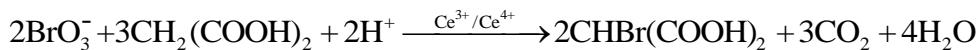


Figure 8.1. Limit cycle attractor in the ‘Oregonator’ model.

Overall the B-Zh reaction may be presented approximately as follows:

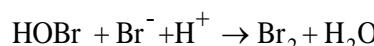
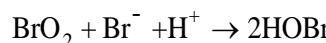
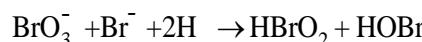


The FKN mechanism for the B-Zh reaction includes three ingredients for which oscillations are observed: 1) the activator, HBrO_2 , that itself provides for its own catalytic formation, as a result of a sequence of reactions (positive feedback); 2) the inhibitor, Br^- , which prevents the autocatalysis with HBrO_2 (negative feedback); and 3) the catalyst that interconverts from the oxidized form into the reduced one (Ce^{4+} and Ce^{3+}).

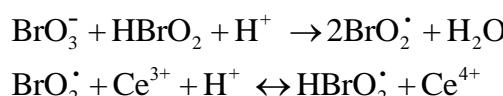
The competition between the three distinctive chemical sequence (A,B,C) ensures the stability of the chemical oscillations.

- Sequence (A) – *absorption of the inhibitor*, bromide ion. Over the induction period of the reaction this ion converts into different oxidized forms (activators).
- Sequence (B) – *autocatalysis* (branching). During this sequence the autocatalysis (reproduction with increase) of the activator, HBrO_2 , takes place. It is established that the autocatalytic formation of HBrO_2 starts when the concentration of Br^- reaches a critical minimum [31]. During this sequence likewise the oxidation of the Ce^{3+} catalyst into Ce^{4+} takes place.
- Sequence (C) – *regeneration of the inhibitor*, Br^- . This sequence is accompanied by the oxidation of the organic substrate, MA, and the reduction of Ce^{4+} into Ce^{3+} . It should be noted that this sequence provides for delay in the inhibitor formation, necessary for the generation of oscillations.

In the framework of the FKN mechanism the sequence (A) is expressed by the following reactions:



The autocatalytic (branching) formation of HBrO_2 and the oxidation of Ce^{3+} (sequence (B)) take place as a result of the following basic reactions:



The overall branching reaction of the $1 \rightarrow 2$ type is as follows:



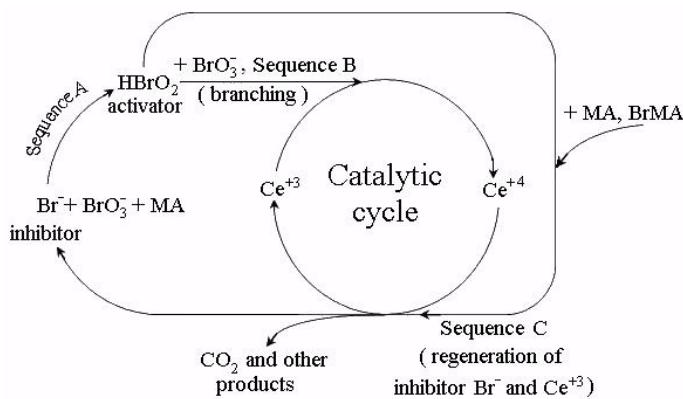


Figure 8.2. Simplified schematic version of the B-Zh reaction.

Regeneration of the inhibitor Br^- (sequence (C)) occurs by a sequence of reactions comprising MA , BrMA , Ce^{4+} and the other active intermediates. This complicated process integrally may be written down in the form of the overall stoichiometry:



where f is the stoichiometric coefficient.

In the scheme shown in Figure 8.2 chemical transformations during the B-Zh reaction are presented in a simplified version.

So we may conclude that a chemical reaction system that includes the steps of autocatalysis and has a time-delayed autoinhibition, under certain conditions could be coherent. It is remarkable that a strict time- and space-ordered complex chemical process is implemented under conditions when its individual chemical steps are of chaotic (disordered) nature.

8.2.2. Kinetic Models of the Belousov-Zhabotinsky Reaction

Analyzing the FKN kinetic scheme for the B-Zh reaction, Field and Noyes [20] from the University of Oregon suggested a simplified realistic (skeletal) model, consisting of the five most important steps. This model, known as the 'Oregonator' [21] reflects the main features of the B-Zh reaction. In one version of the model by Tyson [23,24] the interpretation is presented as follows:

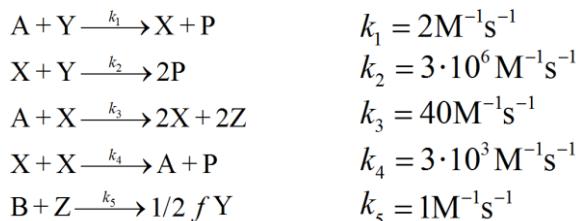


Table 8.1. Reduced EFN mechanism for the self-oscillation oxidation of malonic acid by bromate ion in the presence of cerium ions [29]

No	Reactions	Rate constants*
1	$2H^+ + Br^- + BrO_3^- \rightarrow HOBr + HBrO_2$	2.1
2	$H^+ + HBrO_2 + Br^- \rightarrow 2HOBr$	$2.0 \cdot 10^9$
3	$HBrO_2 + BrO_3^- + H^+ \rightarrow 2BrO_2^\cdot + H_2O$	$1.0 \cdot 10^4$
4-5	$BrO_2^\cdot + Ce^{3+} + H^+ \leftrightarrow Ce^{4+} + HBrO_2$	$6.5 \cdot 10^5, 2.4 \cdot 10^7$
6	$Ce^{4+} + CH_2(COOH)_2 \rightarrow CH(COOH)_2 + Ce^{3+} + H^+$	1.0
7	$CH(COOH)_2 + Br^- + CH_2(COOH)_2 + H_2O \rightarrow Br^- + CH_2(COOH)_2 + HO C(COOH)_2 + H^+$	$1.0 \cdot 10^4$
8	$HOBr + CH_2(COOH)_2 \rightarrow BrCH(COOH)_2 + H_2O$	$6.55 \cdot 10^7$
9	$Ce^{4+} + O=CHCOOH \rightarrow O=CCOOH + Ce^{3+} + H^+$	$5.0 \cdot 10^{-1}$

* Rate constants are presented in units of M, s.

In the ‘Oregonator’ kinetic model the symbolic representations have specific chemical meaning. A \equiv BrO₃⁻, B \equiv MA are the initial reagents, X \equiv HBrO₂, Y \equiv Br⁻, Z \equiv Ce⁴⁺ are the intermediate species, P \equiv HBrO is the reaction product, and *f* is the stoichiometric coefficient indicating how many bromine ions are formed to reduce two cerium ions. According to Tyson [24] the condition $f \in (0.5; 1 + \sqrt{2})$ is the mandatory but not the only sufficient condition for the appearance of oscillations. The irrational number $1 + \sqrt{2}$ obviously cannot be the quantity of ions, however it should be reminded that the ‘Oregonator’ is predominately a mathematical model and the value of *f* is obtained analytically.

In general, the skeletal ‘Oregonator’ model or the ‘Oregonator’-like models describe the experimental data. Nevertheless the precise description of the experimental results is achieved when more extended kinetic models for the B-Zh reaction are used (see, for example [27-32]). At that the propagation of chemical waves in the reactor space (spatial periodicity) is described by the diffusion equations [48-50].

To describe the dynamic behavior of the B-Zh reaction on the basis of the ‘Oregonator’ kinetic model both the analytical [22-26] and numerical [27-30,33-47] methods are used. One of the main findings of these studies is that the inhibitor, bromide ion, controlling the coherence of the B-Zh reaction, plays the role of the “governing variable”. As a remarkable fact it should be stated that, when using the bifurcation theory as a method to identify the instability, in the framework of the ‘Oregonator’ skeletal model, one can succeed in defining the boundaries for the transition of the B-Zh reaction, from one dynamic regime to another, depending on the reaction initial parameters [32,42-47].

When a preliminary extended version of the kinetic model is used to identify the B-Zh reaction mechanism, frequently classical approximation methods are used, such as the rate-determining step and the quasi-steady state approximations (see, for example [22,24-26]). However T. Turanyi and S. Vajda [29], applying the sensitivity analysis method, more precisely the method of the “principal components analysis” selection, specified numerically a base mechanism that comprise only 9 steps for the B-Zh reaction (see table 8.1), from the conventional model of Edelson-Field-Noes (EFN), which includes 32 steps. In this case, the

reduction of the mechanism has not resulted in significant loss of accuracy of its descriptive capability. Note that the EFN mechanism for the B-Zh reaction is somewhat the extended version of the FKN mechanism. The applied numerical method undoubtedly is more promising, as it allows to reject correctly the inessential steps from the sufficiently extended version of the mechanism.

8.3. NUMERICAL VALUE IDENTIFICATION AND ANALYSIS OF CRITICAL CONDITIONS FOR NONLINEAR DYNAMIC CHEMICAL SYSTEMS

As mentioned above, identifying the boundaries for the transition of one dynamic regime of a nonlinear reaction system to another is very important. Here it is necessary to develop new efficient numerical methods, enabling to solve such tasks for sufficiently complicated multistep chemical models. The *value* approach, as in the case of the identification of critical conditions for branching chain reactions (see Chapter 5), seems to be an effective tool in identifying the regions of manifestation for one or another dynamic regime, in the chemical reaction phase diagram. Here also is possible a rigorous identification of the roles of individual steps in the reaction mechanism for different regimes of dynamic behavior.

Calculational Procedure

Transition from one dynamic regime to another is critical, as it demonstrates high sensitivity to the initial conditions of reactions. For this reason, by analogy with the branching chain reactions (see Section 5.4), an extremal behavior of concentrations or the sum of concentrations for the reaction ingredients is suggested as the criterion for the critical state of a nonlinear dynamic system [51-53]. For the numerical calculation of the initial reaction conditions satisfying the suggested criterion, here likewise one of the versions of variational calculus, Pontryagin's principle of maximum [54,55] with the *value* identification of the roles of individual steps for reaction mechanism, was used. In accordance with the selected criterion, the critical state of a reaction system is formulated as:

$$I(t) = \int_0^t \sum_{i=1}^m f_i dt \rightarrow \text{extremum} \quad (8.1)$$

where f_i is the rate-of-production of the i -th species, and t is the time.

To find the initial conditions of the reaction for which the critical condition (8.1) is realized, the kinetic equations for individual species are formalized by the Hamiltonian as described in Chapter 4. So, the Hamiltonian H serves as an "indicator" for the realization of condition (8.1), depending on the initial conditions of a reaction (\mathbf{u}). Under critical conditions the Hamiltonian H^* achieves the extremum:

$$H(\mathbf{u}^*) = \sup_{\mathbf{u}} H(\mathbf{u}) = 0. \quad (8.2)$$

As noted in Chapter 5, under given conditions of the reaction, the Hamiltonian is constant over time, i.e. during the entire chemical conversion the condition $H(t) = \text{const}$ is maintained throughout the entire process of a chemical transformation. Thereby, the numerical analysis for the behavior of H value depending on the initial parameters is possible to perform at the initial stage of a reaction (at $5 \cdot 10^{-2}$ s). And this simplifies the calculations cardinally, which is an important point.

There exists one more specific feature of the Hamiltonian formalism in the *value* interpretation (see Chapters 3 and 4). Namely, it allows to identify the role of individual chemical steps under the critical conditions of a reaction [51-53]. Conceptually here a cause-and-effect relation is revealed in the critical changeover of the dynamic behavior for a nonlinear reaction system.

The capabilities of the suggested method for studying the nonlinear dynamic systems are demonstrated by the example of the above-mentioned ‘Oregonator’ skeletal model, describing the B-Zh reaction. To simulate an open reaction system the concentrations for A and B were kept constant with time. For calculations the extremal behavior of concentration for the activator X was adopted as a critical condition:

$$I(t) = \Delta[X(t)] = \int_0^t f_X dt \rightarrow \text{extremum} \quad (8.3)$$

8.4. DYNAMIC REGIMES OF THE BELOUSOV-ZHABOTINSKY REACTION ACCORDING TO THE “OREGONATOR” KINETIC MODEL

As shown in Figure 8.3, the concentrations for the three intermediates (X,Y,Z) exhibit an oscillating behavior at certain initial concentrations of reaction species.

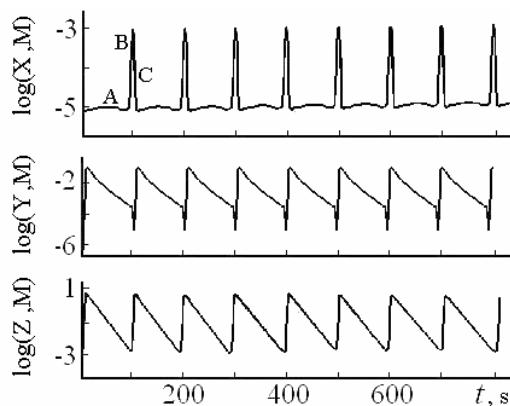


Figure 8.3. Quasiperiodic oscillation regime for the reaction intermediates according to the ‘Oregonator’ kinetic model.

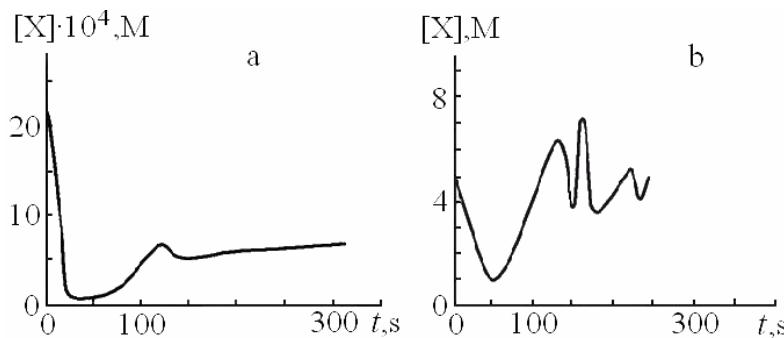


Figure 8.4. Stationary (a) and chaotic (b) oscillation modes for the concentration of the species X.

Oscillations of the reaction system shown in Figure 8.3 are well reproducible at least for the first nine oscillation periods. Note that the oscillation period ($T \sim 100$ s) is close to the magnitudes observed experimentally for the B-Zh reaction (300-600 s). When changing the values of initial concentrations of reaction species, the calculations predict both the stationary and chaotic modes of the reaction (as shown in Figure 8.4).

8.5. PHASE DIAGRAM

Figure 8.5 demonstrates the calculated phase diagram for the ‘Oregonator’ kinetic model, describing the dynamic behavior of the system in coordinates of the initial concentrations $[A]_0$ and $[Y]_0$. The phase diagram comprises the zones of different reaction modes: for the quasiperiodic oscillations, the stationary mode and the chaotic damped oscillations.

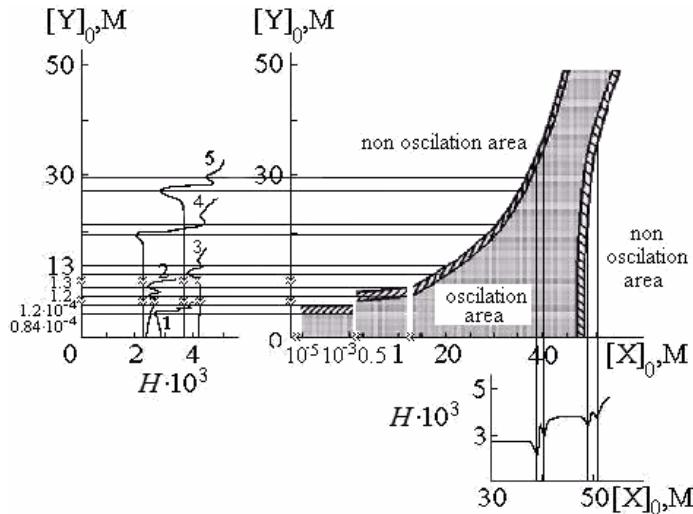


Figure 8.5. Phase diagram of the ‘Oregonator’ kinetic model for the B-Zh reaction, indicating different modes of the reaction, depending on the magnitudes of initial concentrations $[X]_0$ (HBrO_2) and $[Y]_0$ (Br^-). Dependences of the Hamiltonian on $[X]_0$ and $[Y]_0$ for the reaction time $t = 0.05$ s, $[\text{BrO}_3]_0 = 10^{-2}$ M, $[\text{MA}]_0 = 0.3$ M, $[\text{Ce}^{4+}]_0 = 0.384$ M are also shown.

It should be noted that the range of experimentally unrealizable concentrations $[X]_0$ and $[Y]_0$, far exceeding the value 10 M, was also intentionally studied. This was to test the capabilities of the *value* approach for determining the boundaries between different reaction modes, within a wide range of variation of the initial parameters. It follows from the results presented in Figure 8.5 that there exists a relatively narrow band of chaotic-damped oscillations, between the zones of the quasiperiodic oscillations and the stationary mode of the reaction. Transition of the reaction modes is critical, i.e. it takes place at relatively small changes in the initial reaction parameters, in this case in $[X]_0$ and $[Y]_0$. The suggested criterion for the critical reaction conditions (equations 8.1 and 8.3) accurately predicts the critical changeover of the reaction modes. As Figure 8.5 shows, in strict accordance with the selected criterion of critical reaction conditions, the extremal values of the Hamiltonian fit to them. In this case, the condition $\partial H/\partial u = 0$ is met, where $u = [X]_0$ or $u = [Y]_0$. So, the extrema of the Hamiltonian reliably predict the changeover of the dynamic modes of the reaction, when $[X]_0$ is the argument at different initial values of $[Y]_0$, similar to the case when $[Y]_0$ is the argument. Also, it should be noted that in some cases the local extrema of H are observed within the zone of a chaotic reaction. Apparently, its nature is complicated and requires a separate investigation.

8.6. DYNAMICS OF KINETIC SIGNIFICANCES FOR INDIVIDUAL STEPS

As already mentioned, the *value* analysis allows to identify numerically the dynamics of relative significances for individual steps of reaction mechanism, which is very important. Previously the role of individual steps for the B-Zh reaction was identified, by the method of sensitivity analysis of output characteristics of the reaction, to variations in the values of the rate constants of these steps [25-28]. We believe the *value* identification of significances for individual steps in time will complement the information about them, because according to equation (3.3) the *values*, by definition, are somewhat different from the local sensitivities S .

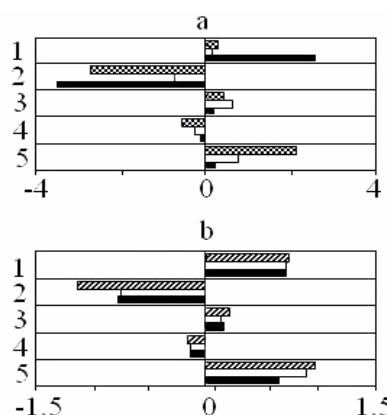


Figure 8.6. *Value* contributions of individual steps of the 'Oregonator' kinetic model for the B-Zh reaction at (a) the quasiperiodic oscillation reaction mode: \blacksquare sequence A (40s), \square sequence B (75s), \blacksquare sequence C(92s) and (b), the stationary mode: \blacksquare 110s, \square 120s, \blacksquare 130s. The numbers in this Figure correspond to that of the steps in the 'Oregonator' kinetic model.

Value contributions for harmonic oscillations corresponding to the above-mentioned sequences A, B and C, as well as at a stationary reaction mode are illustrated in Figure 8.6. As during the reaction (1) presented in Table 8.1, the consumption of Br^- yields the activator X (HBrO_2), where its *value* contribution is positive. In sequence A, as expected, the most important role is played by reaction (1) and (2), leading to the consumption of the inhibitor, the Br^- ion, while the role of the autoinitiation reaction (3) is not important.

Now let us specify the role of individual steps in sequence B. In the autoinitiation stage the role of reaction (1) and (2) responsible for the inhibitor, Br^- , consumption decreases significantly, and the opposite is true for the autoinitiation sequence (3), ensuring the positive feedback.

When regeneration of the inhibitor Br^- and the catalyst Z (sequence C) takes place, then reaction (5), which yields these two reaction species plays an important role. Therewith the role of reaction (2), which inhibits the process due to quadratic loss (interaction) of the activator X (HBrO_2) becomes more important.

In the stationary mode the process is mainly controlled by the inhibition step (2) and step (5) results in the formation of the inhibitor Y (Br^-) and the catalyst Z. Also one can see that the changes in the time dependences of the absolute *value* contributions of the steps in the stationary mode are much smaller than in the oscillation mode. Most likely, this is due to the fact that an abrupt change in the concentration of substances, consequently in the step rates, result in similar changes in the role of steps.

We summarize our findings. It is suggested the criterion of critical condition, that is, the extremal behavior of the reaction species' concentration, may be applied to reveal the critical conditions of nonlinear chemical dynamic systems. This is with the changeover of different dynamic modes of the reactions, such as the quasi-periodic and chaotic oscillations of the intermediate concentrations, as well as the steady-state mode. At the same time the Hamiltonian formalism makes it possible not only to have a successful numerical identification of the critical reaction conditions, but also to specify the role of individual steps of the reaction mechanism under different conditions.

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Chapter 9

VALKIN: A SOFTWARE PACKAGE FOR THE KINETIC ANALYSIS OF REACTION SYSTEMS BY THE *VALUE* METHOD

In this chapter the computer program package VALKIN for the kinetic analysis of reaction mechanisms by the *value* method is described. In this program, the system of kinetic and conjugate equations is numerically integrated by a modified variant of the Runge - Kutt method. The program is designed to solve the "stiff" ordinary differential equations, inherent in the problems of chemical kinetics and control. The maximum number of individual steps, chemical species and fixed time points are 1000, 300 and 6000, respectively. At the same time, this program allows to increase significantly these numerical indicators. Calculated data are written in Microsoft EXCEL format. The program calculates both the isothermal and non-isothermal reaction modes.

The kinetic computer program package VALKIN structurally consists of the main program and several subprograms. The main program processes the input and output database, and communicates with the subprograms. The system of differential equations is composed and numerical integration is performed with subprograms. Simultaneously, the output reaction characteristics are calculated, yielding the kinetic path of species concentrations, the rates of individual steps, the *values* and *value* contributions of the species and the individual steps in reaction mechanisms, as well as the Hamiltonian quantity.

In the input data of the software the characteristics of a reaction's kinetic model are presented, including the initial chemical species, the number of species and the individual steps. Simultaneously, the number of fixed points in time and their quantities are given. In the input data the parameters of integration, including the accuracy of integration steps, as well as the initial quantities of the concentrations of the reaction species and the conjugate functions are also provided. The target functional for the chemical reaction is given essentially by the initial quantities of conjugate functions. For the calculations performed in the non-isothermal reaction conditions given are the initial temperature, the heat capacity of the reaction mixture, and the reactor characteristics: the volume, the inner surface of the reactor, the temperature and the thermal conductivity of the reactor wall.

The facts stated in this book allow to draw a conclusion that the modeling of multistep chemical reactions has a key role in chemical kinetics. It should be reminded once more that modeling the reaction system includes the following computational procedures:

- compiling the kinetic equations for the reaction mechanism and their solution;
- comparing the calculation data with experimental results;
- identifying the level of influence of kinetic parameters on the obtained results;
- reducing the reaction mechanism; identifying the role, the kinetic significances of individual steps and the species of a complex chemical reaction; the optimal control of chemical reactions, etc.

It should be emphasized that numerical calculations that enable the predicting of steps and species of the reaction, with which the latter may be efficiently controlled, represent a new and promising trend in chemical investigations. As mentioned above, one of the consequences of such an approach is the opportunity to define the molecular structure of the complex reaction's efficient stimulators and inhibitors.

Development of the computing techniques in accordance with the problems defined above and their correlation with other existing computing methods is in many respects the prerequisite to achieve success in such calculations.

Here, we should make the following comment. Noteworthy, most chemists starting studies in this field, in general are not familiar with the relevant mathematical methods and the details of computer software. This, in turn, causes certain difficulties in analyzing the obtained results. In our opinion, the added complication is in the lack of confidence of many researchers in completely understanding the currently used kinetic software. Surely, successful computations carried out using these programs will serve as a positive factor.

Up-to-date chemical computer software are developed in such a way to make them usable to chemists who may not have the knowledge of the mathematical methods employed in the kinetic computing program and on the ways of their practical application. However, it becomes clear that the last circumstance impedes researchers to respond adequately in "non-standard" situations, for example, when correcting the possible accumulation of errors in kinetic calculations. Obviously, the mentioned factor is of great importance. Nevertheless, it should be recognized that computer applications in chemical kinetics does not allow organizing such a working mode of calculations to overcome all the arising problems automatically. Such problems may be subdivided conventionally into two types, connected with:

- the adequate formulation of the target;
- the capabilities of computer-aided calculations.

Let us discuss each in detail. One of the major challenges facing a researcher, when calculating by the use of the software VALKIN or other kinetic computational programs (for example, those based on the sensitivity analysis method), is the selection of the target functional, the Q-factor of the reaction. This functional must reflect correctly the specified goal (for example, the reaction selectivity, the kinetics of the concentration change for the species of a reaction system, etc.). At the same time, the selected target functional of a chemical reaction does not have to coincide "exactly" with the meaning of a selected goal. We need only to select the functional that strictly describes the target in an extremum condition. This enables to overcome certain difficulties arising at numerical modeling of multistep chemical reactions without losing in the rigor of solution.

In our case, at this stage of solving the task on reaction modeling it is desirable the appropriate Hamiltonian of the reaction system to be linearly dependent on the variable control parameters. This facilitates both the calculation procedure itself and analysis of the data obtained. Therefore, for every particular case the target functional is selected having in mind this factor too.

And finally, as you already know, the target functional of reaction system in the *value* approach is selected subject to the opportunity for defining the “physical, kinetic” meaning of initial values for the function ψ_i , conjugated to concentrations of species, c_i . It should be reminded that this also simplifies considerably the procedure of numerical calculations.

Let us address now the problem related to the capabilities of computer-aided kinetic calculations. But, it should be noted first of all that we don’t mean concerning the capabilities of computers, i.e., their performance, memory size, etc. These parameters are continuously improving and it is hardly probable that they may seriously impede the kinetic calculations. Currently, the basic problem is hidden elsewhere. Thus, when solving the system of kinetic equations the necessity to improve the calculation accuracy leads to increase in the number of mathematical operations. This in turn causes accumulation of errors during calculations. In such way a paradoxical situation may appear. Namely, decreasing in ε value that specifies the accuracy grade of calculations one can enlarge the volume of errors made. On the other hand, the situation is aggravated as the available computer-based kinetic programs are not capable to estimate the credibility level of calculations performed. This primarily is linked with absence of adequate criteria for such computations.

From the aforesaid the following very important problem emerges: assessment of accuracy grade when using either kinetic program. We believe that just this issue requires the active intervention of experts. In most cases for assessment of the computing accuracy grade the following strategy is followed: the obtained calculation data are compared with those for the well-known reaction mechanisms available in the literature. If the calculation data agree well then goal-oriented calculations are carried out by a new method.

Overcoming such difficulty for less studied reaction mechanisms becomes more complicated, and here, undoubtedly, the constructive approach is required.

So, it can be summarized that the kinetic software codes undoubtedly are the powerful tool in hands of researchers, but their usage requires a creative approach. It is not difficult to predict that degree of active manual calculations will decrease considerably over the time.

9.1. DESCRIPTION OF THE VALKIN SOFTWARE

Package of the VALKIN software is intended for the kinetic analysis of the chemical reaction mechanisms. The basic specific features of the software are listed below:

- In this program the system of kinetic equations is solved by Runge-Kutt method [1,2]. Its modified version (B. Gottwald, G. Wanner [3]) is used to solve “stiff” differential equations (the case with broad spectrum of temporal characteristics for species of the reaction system [2]).
- The kinetic VALKIN software is written using the FORTRAN-77 language.

- Maximum numbers for individual steps, chemical species and fixed reaction times are equal to 1000, 300 and 6000, respectively. It should be pointed out that the program enables these numerical characteristics to be raised markedly.
- An important distinguishing feature of the VALKIN software is that apart from determining the concentration change for chemical species over time, it allows also to measure the *values*, $\psi_i(t)$, and the *value* contributions of species, $b_i(t)$, as well as the *values*, $G_j(t)$, the *value* contributions, $h_j(t)$, and the rates, $r_j(t)$, for the individual steps of a reaction, and the magnitude of Hamiltonian H .
- The data obtained by the VALKIN software are recorded in the EXCEL format enabling to use its wide graphic capabilities.

9.2. STRUCTURE OF THE VALKIN SOFTWARE PACKAGE

The structure of the VALKIN software package is demonstrated in Figure 9.1.

- The main program of VALKIN represents a unit, where the database is processed, link is ensured with sub-programs, and the output parameters are arranged.
- Subprograms serve the following functions:
 - compiling the system of differential equations in accordance with the reaction kinetic model,
 - solving the system of “stiff” differential equations,
 - calculation of kinetic trajectories for species concentrations, rates of reaction steps, *values* of species and steps of the reaction mechanism.

It is significant that the VALKIN program enables to use different computational algorithms, which are aimed not only at optimising the computing process, but also at updating the package by means of new algorithms, to make it more comprehensive. As mentioned, calculations presented in this book were carried out using the subprogram ROW-4A [3]. The main reason was an attempt to compare the obtained data with those performed by using other methods, including the sensitivity analysis method, where the mentioned subprogram is primarily used.

9.3. THE INPUT DATA FILE

Prior to the VALKIN program’s start-up it is required to enter the input data. For demonstration we provide a format of the input data file for the kinetic model of the reaction between molecular hydrogen and oxygen consisting of 35 steps [4]. We addressed this reaction in Chapters 1 and 5.

First, the kinetic scheme of the reaction is compiled, followed by goal formulation. The initial task is to calculate the time-dependent change in the concentration of species, at pressure P and temperature T , while dimensions of the reactor are given by the volume V and internal surface S . The reactive medium is also specified by the heat conductivity of reactor walls.

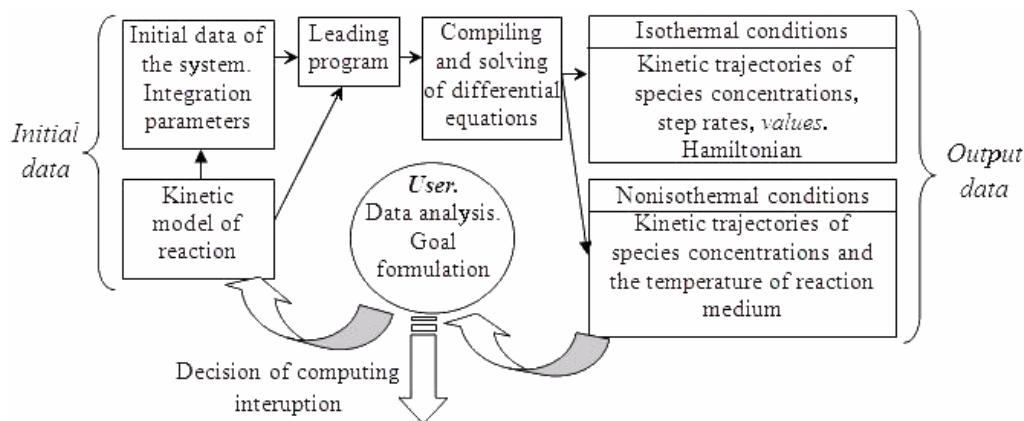


Figure 9.1. Formalized scheme of procedures of the VALKIN software package for the analysis of reaction mechanisms.

In VALKIN the condition $Cizo=1$ corresponds to nonisothermal, and $Cizo= -1$ for isothermal conditions of the reaction. Obviously, formulating the reaction mechanism requires the values of the rate constants for individual steps. For nonisothermal conditions, the parameters specifying the rate constant of a step (k^0, n, E) by the Arrhenius equation, (9.1), as well as the values of thermal effects of steps, $\Delta H_j^0, j=1,2,\dots,n$ are given, with

$$k = k^0 T^n \exp(-E/RT) \quad (9.1)$$

In the case under consideration, the objective is to reveal the influence of individual steps on the kinetics of hydrogen peroxide accumulation. On this basis initial *values* for the reaction species, $\psi_i(t_0)$: 1, for hydrogen peroxide, and 0, for the remaining species are selected.

Files of input data for nonisothermal and isothermal conditions of the reaction appear in Table 9.1 (italics denote author's comments).

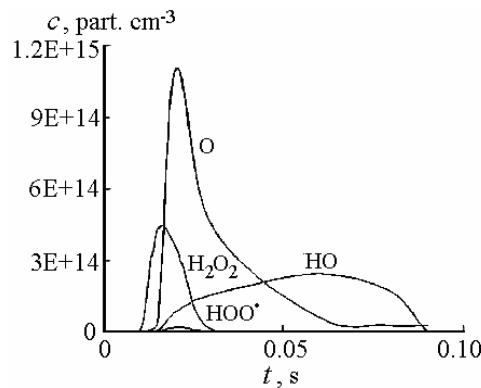


Figure 9.2. Concentration profiles of H_2O_2 , HOO^\bullet , O , HO^\bullet vs time for the reaction of hydrogen with oxygen.

Table 9.1. Initial file (INPUT FILE) of calculation, Y denotes $\psi_i(t_0)$

INPUT DATA	
N 1	2H2+O2 (<i>Initial species of reaction</i>)
9	NUMBER OF SPECIES (<i>Number of reaction species</i>)
35	NUMBER OF REACTIONS (<i>Number of individual steps</i>)
49	NUMBER OF PRINT POINTS (<i>Number of fixed time steps for which output data are given</i>)
0.1e-11	H (<i>Initial step of integration</i>)
1.00e-1	HMAX (<i>Maximum step of integration</i>)
0.1e-5	EPS (<i>Accuracy of integration step</i>)
730.	TEMPERATURE (K) (<i>Temperature of reaction mixture, K</i>)
0.008314	GAS CONSTANT (J/mol*K*1000)
1.	Cizo (<i>Index of reaction isothermicity</i>)
0.0254	Cv (<i>Heat capacity at constant volume</i>)
2.7e-6	Alfa (<i>Heat conductivity factor of the reactor walls</i>)
150.72	S (<i>Internal surface of the reactor, cm²</i>)
150.72	V (<i>Reactor volume, cm³</i>)
730.	Ts (K) (<i>Temperature of the reactor's wall, K</i>)
<i>Initial magnitudes of reaction species values</i>	
YH	0.0
YO	0.0
YHO	0.0
YHO2	0.0
YO2	0.0

YH2	0.0
YH2O	0.0
YH2O2	1.0
YM	0.0

Fixed time steps (s), for which output data are given

0.00E+00	3.00E-10	3.00E-09	3.00E-08	3.00E-07	5.00E-07	7.00E-07		
9.00E-07	1.00E-06	3.00E-06	5.00E-06	7.00E-06	8.00E-06	9.00E-06		
1.00E-05	3.00E-05	4.00E-05	4.00E-05	6.00E-05	7.00E-05	8.00E-05		
9.00E-05	1.00E-04	2.00E-04	3.00E-04	4.00E-04	5.00E-04	6.00E-04		
7.00E-04	8.00E-04	9.00E-04	1.00E-03	2.00E-03	3.00E-03	4.00E-03		
5.00E-03	7.00E-03	8.00E-03	9.00E-03	1.00E-02	1.70E-02	2.00E-02		
2.50E-02	3.00E-02	8.00E-02	9.00E-02	3.00E-00	5.00E-00	7.00E-00		

1.,16.,17.,33.,32.,2.,18.,34. (Atomic and molecular masses of reaction species)

H	O	HO	HO2	O2	H2	H2O	H2O2	M. (Reaction species)
---	---	----	-----	----	----	-----	------	-----------------------

REACTION LIST (Reaction mechanism)

<i>Initial species</i>				<i>Reaction products</i>				
1	H ₂ O ₂	M		HO	HO	M		
2	HO	HO	M	H ₂ O ₂	M			
3	H ₂	HO		H ₂ O	H			
4	H	H ₂ O		H ₂	HO			
5	H	O ₂		OH	O			
6	HO	O		H	O ₂			
7	O	H ₂		HO	H			
8	HO	H		O	H ₂			

Table 9.1. (Continued)

9	H	O ₂	M	HO ₂	M			
10	HO ₂	M		H	O ₂	M		
11	HO	HO		H ₂ O	O			
12	O	H ₂ O		HO	HO			
13	H	H	M	H ₂	M			
14	H ₂	M		H	H	M		
15	O	O	M	O ₂	M			
16	O ₂	M		O	O	M		
17	OH	H	M	H ₂ O	M			
18	H ₂ O	M		H	HO	M		
19	H	HO ₂		HO	HO			
20	HO	HO		H	HO ₂			
21	H ₂ O ₂	HO		HO ₂	H ₂ O			
22	HO ₂	H ₂ O		H ₂ O ₂	HO			
23	HO ₂	HO ₂		H ₂ O ₂	O ₂			
24	H ₂ O ₂	O ₂		HO ₂	HO ₂			
25	O	H ₂ O ₂		H ₂ O	O ₂			
26	O ₂	H ₂ O		O	H ₂ O ₂			
27	H	H ₂ O ₂		HO ₂	H ₂			
28	H ₂	HO ₂		H	H ₂ O ₂			
29	O	H ₂ O ₂		HO	HO ₂			
30	HO	HO ₂		O	H ₂ O ₂			

31	H	H ₂ O ₂		H ₂ O	HO			
32	HO	H ₂ O		H	H ₂ O ₂			
33	O ₂	H ₂ O		HO ₂	HO			
34	HO	HO ₂		O ₂	H ₂ O			
35	H ₂	O ₂		HO	HO			

Initial concentrations of reaction species (part.· cm⁻³)

H	0.00E+00
O	0.00E+00
HO	0.00E+00
H ₂	4.46E+17
O ₂	2.23E+17
HO ₂	0.00E+00
H ₂ O	0.00E+00
H ₂ O ₂	0.00E+00
M	6.69E+17

REACTION RATE CONSTANTS: *Arrhenius parameters (k⁰, n, E) of rate constants and enthalpy change ΔH⁰ of elementary reactions*

	<i>k⁰ (cm³, part., s)</i>	<i>n</i>	<i>E (kJ/mol)</i>	<i>ΔH 0 (kJ/mol)</i>				
1	6.75E-08	0.	175.0	208.0				
2	1.20E-30	0.	0.0	-208.0				
3	4.00E-11	0.	21.6	-62.5				
4	3.20E-11	0.	72.9	62.5				
5	1.30E-10	0.	66.5	71.0				

Table 9.1. (Continued)

6	5.00E-11	0.	5.0	-71.0				
7	4.20E-12	0.	32.1	8.3				
8	1.00E-11	0.	31.2	-8.3				
9	5.00E-33	0.	0.0	-196.0				
10	2.80E-09	0.	205.0	196.0				
11	2.40E-11	0	0.0	-71.0				
12	2.70E-10	0.	75.8	71.0				
13	1.00E-32	0.	0.0	-430.0				
14	9.15E-08	0.	436.0	430.0				
15	5.00E-33	0.	0.0	-492.0				
16	2.50E-07	0.	500.0	492.0				
17	1.00E-31	0.	0.0	-492.0				
18	1.00E-20	0.	0.0	500.0				
19	1.00E-11	0.	0.0	-154.0				
20	8.00E-13	0.	157.0	154.0				
21	1.30E-11	0.	6.7	-129.0				
22	1.00E-13	0.	129.0	129.0				
23	4.00E-11	0.	6.3	-167.0				
24	1.00E-10	0.	167.0	167.0				
25	4.70E-11	0.	26.9	-178.5				
26	8.00E-11	0.	383.9	178.5				
27	1.20E-11	0.	17.6	-67.2				

28	2.70E-06	0.	84.0	67.2				
29	4.70E-11	0.	26.9	-58.8				
30	4.80E-12	0.	85.7	58.8				
31	3.70E-09	0.	49.6	-232.6				
32	4.00E-10	0.	340.2	232.6				
33	1.25E-13	0.5	307.4	243.6				
34	8.70E-14	0.5	89.0	-243.6				
35	1.38E-10	0.	188.5	77.9				

*END

It follows from Table 9.1. that the file of initial data of the kinetic VALKIN software is distinguished by compactness and is user-friendly.

9.4. COMPUTING DATA UNDER REACTION NONISOTHERMAL CONDITIONS AND THEIR GRAPHIC PRESENTATION

Computing data are recorded in files OUTT and GRAFT. Figures 9.2 and 9.3 illustrate the data for the mechanism of the reaction between hydrogen and oxygen obtained by processing the file GRAFT using the EXCEL program.

It is worth noting that the computing data under nonisothermal conditions, along with the kinetic curves of chemical species, include also the time-dependence of the temperature of the reaction medium.

9.5. COMPUTED VALUES UNDER REACTION ISOTHERMAL CONDITIONS

Computing *value* magnitudes are recorded in files OUT and GRAF. For the mechanism of the reaction between hydrogen and oxygen the file with appropriate calculated data is presented in Figures 9.5 and 9.6.

The results of computing by using VALKIN are generated in text and graphical forms. An example of calculated text is shown in Table 9.2.

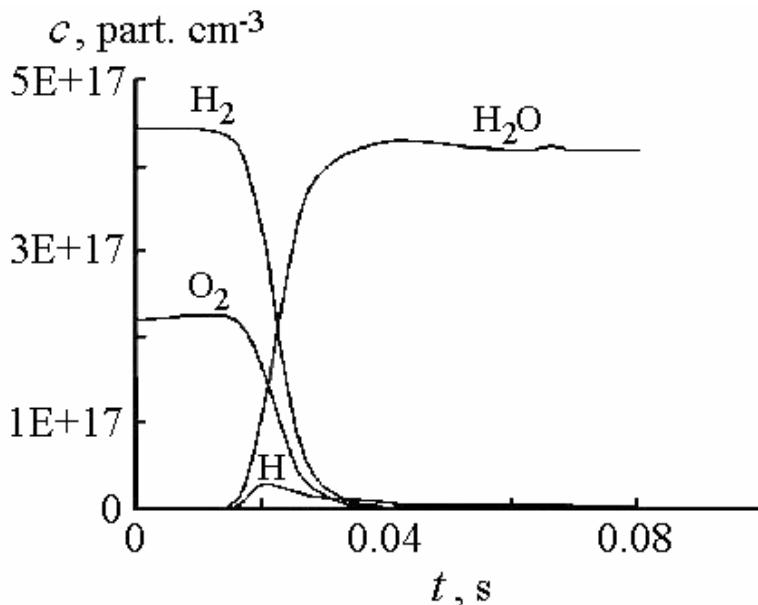


Figure 9.3. Concentration profiles for H₂, O₂, H₂O, H vs time for the reaction of hydrogen with oxygen.

Table 9.2. Computed output parameters for the reaction between hydrogen and oxygen

N 2	H2+O2						
.1000000E-11	.1000000.	1000000E-05	730.0000	.8314000E-02			
Cizo	-1.000000						
Cv	.2540000E-01						
Alfa	.2700000E-05						
S	150.7200						
V	150.7200						
Ts (K)	730.0000						
YH	.0000000						
YO	.0000000						
YHO	.0000000						
YHO2	.0000000						
YO2	.0000000						
YH2	.0000000						
YH2O	.0000000						
YH2O2	1.0000000						
YM	.0000000						
.00E+00	.30E-09	.30E-08	.30E-07	.30E-06	.50E-06	.70E-06	
.90E-06	.10E-05	.30E-05	.50E-05	.70E-05	.80E-05	.90E-05	
.10E-04	.30E-04	.40E-04	.40E-04	.60E-04	.70E-04	.80E-04	
.90E-04	.10E-03	.20E-03	.30E-03	.40E-03	.50E-03	.60E-03	
.70E-03	.80E-03	.90E-03	.10E-02	.20E-02	.30E-02	.40E-02	
.50E-02	.70E-02	.80E-02	.90E-02	.10E-01	.17E-01	.20E-01	
.25E-01	.30E-01	.80E-01	.90E-01	.30E+01	.50E+01	.70E+01	

Table 9.2. (Continued)

1.0	16.0	17.0	33.0	32.0	2.0	18.0	34.0
***** OUTPUT REACT *****							
REACTION LIST							
1		$H_2O_2 + M = HO + HO + M$					
2		$HO + HO + M = H_2O_2 + M$					
3		$H_2 + HO = H_2O + H$					
4		$H + H_2O = H_2 + HO$					
5		$H + O_2 = HO + O$					
6		$HO + O = H + O_2$					
7		$O + H_2 = HO + H$					
8		$HO + H = O + H_2$					
9		$H + O_2 + M = HO_2 + M$					
10		$HO_2 + M = H + O_2 + M$					
11		$HO + HO = H_2O + O$					
12		$O + H_2O = HO + HO$					
13		$H + H + M = H_2 + M$					
14		$H_2 + M = H + H + M$					
15		$O + O + M = O_2 + M$					
16		$O_2 + M = O + O + M$					
17		$HO + H + M = H_2O + M$					
18		$H_2O + M = H + HO + M$					
19		$H + HO_2 = HO + HO$					
20		$HO + HO = H + HO_2$					
21		$H_2O_2 + HO = HO_2 + H_2O$					
22		$HO_2 + H_2O = H_2O_2 + HO$					

23	$\text{HO}_2 + \text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2$							
24	$\text{H}_2\text{O} + \text{O}_2 = \text{HO}_2 + \text{HO}$							
25	$\text{O} + \text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{O}_2$							
26	$\text{O}_2 + \text{H}_2\text{O} = \text{O} + \text{H}_2\text{O}_2$							
27	$\text{H} + \text{H}_2\text{O}_2 = \text{HO}_2 + \text{H}_2$							
28	$\text{H}_2 + \text{HO}_2 = \text{H} + \text{H}_2\text{O}_2$							
29	$\text{O} + \text{H}_2\text{O}_2 = \text{OH} + \text{HO}_2$							
30	$\text{HO} + \text{HO}_2 = \text{O} + \text{H}_2\text{O}_2$							
31	$\text{H} + \text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{HO}$							
32	$\text{HO} + \text{H}_2\text{O} = \text{H} + \text{H}_2\text{O}_2$							
33	$\text{O}_2 + \text{H}_2\text{O} = \text{HO}_2 + \text{HO}$							
34	$\text{HO} + \text{HO}_2 = \text{O}_2 + \text{H}_2\text{O}$							
35	$\text{H}_2 + \text{O}_2 = \text{HO} + \text{HO}$							
SPECIES LABELS INPUT IN LIST								
H	O	HO	HO2	O2	H2	H2O	H2O2	M
***** END REACT *****								
NUMBER OF REACTIONS (NR) 35								
NUMBER OF SPECIES (NS) 9								
NUMBER OF SPECIES VARIED (NV) 9								
INITIAL CONCENTRATIONS								
H	0.0000D+00							
O	0.0000D+00							
HO	0.0000D+00							
HO2	0.0000D+00							
O2	2.2300D+17							
H2	4.4600D+17							
H2O	0.0000D+00							

Table 9.2. (Continued)

H2O2	0.0000D+00						
M	6.6900D+17						
TEMPERATURE 730.00							
REACTION RATE CONSTANTS (cm^3 , part., s)							
	k	n	E	ΔH^0			
1	2.0270D-20	0.0000D+00	1.7500D+02	2.0800D+02			
2	1.2000D-30	0.0000D+00	0.0000D+00	-2.0800D+02			
3	1.1388D-12	0.0000D+00	2.1600D+01	-6.2500D+01			
4	1.9438D-16	0.0000D+00	7.2900D+01	6.2500D+01			
5	2.2668D-15	0.0000D+00	6.6500D+01	7.1000D+01			
6	2.1937D-11	0.0000D+00	5.0000D+00	-7.1000D+01			
7	2.1197D-14	0.0000D+00	3.2100D+01	8.3000D+00			
8	5.8536D-14	0.0000D+00	3.1200D+01	-8.3000D+00			
9	5.0000D-33	0.0000D+00	0.0000D+00	-1.9600D+02			
10	5.9979D-24	0.0000D+00	2.0500D+02	1.9600D+02			
11	2.4000D-11	0.0000D+00	0.0000D+00	-7.1000D+01			
12	1.0171D-15	0.0000D+00	7.5800D+01	7.1000D+01			
13	1.0000D-32	0.0000D+00	0.0000D+00	-4.3000D+02			
14	5.7892D-39	0.0000D+00	4.3600D+02	4.3000D+02			
15	5.0000D-33	0.0000D+00	0.0000D+00	-4.9200D+02			
16	4.1639D-43	0.0000D+00	5.0000D+02	4.9200D+02			
17	1.0000D-31	0.0000D+00	0.0000D+00	-4.9200D+02			
18	9.9566D-42	0.0000D+00	5.0300D+02	4.9200D+02			
19	1.0000D-11	0.0000D+00	0.0000D+00	-1.5400D+02			
20	4.6629D-24	0.0000D+00	1.5700D+02	1.5400D+02			

21	4.3103D-12	0.0000D+00	6.7000D+00	-1.2900D+02			
22	5.8771D-23	0.0000D+00	1.2900D+02	1.2900D+02			
23	1.4166D-11	0.0000D+00	6.3000D+00	-1.6700D+02			
24	1.1220D-22	0.0000D+00	1.6700D+02	1.6700D+02			
25	5.5875D-13	0.0000D+00	2.6900D+01	-1.7850D+02			
26	2.7065D-38	0.0000D+00	3.8390D+02	1.7850D+02			
27	6.6036D-13	0.0000D+00	1.7600D+01	-6.7200D+01			
28	2.6338D-12	0.0000D+00	8.4000D+01	6.7200D+01			
29	5.5875D-13	0.0000D+00	2.6900D+01	-5.8800D+01			
30	3.5385D-18	0.0000D+00	8.5700D+01	5.8800D+01			
31	1.0447D-12	0.0000D+00	4.9600D+01	-2.3260D+02			
32	1.8130D-34	0.0000D+00	3.4020D+02	2.3260D+02			
33	3.4040D-34	5.0000D-01	3.0740D+02	2.4360D+02			
34	1.0060D-18	5.0000D-01	8.9000D+01	-2.4360D+02			
35	4.4813D-24	0.0000D+00	1.8850D+02	7.7900D+01			

Initial pressure (torr) 5.1220D+01 (*initial pressure of reaction system*)

Time : 1.0000D-02 (*reaction time, s*)

Concentrations: (*for reaction species, part.cm⁻³*)

H	= 8.696D+12	O = 4.235D+11	OH = 1.664D+10				
HO2	= 5.562D+09	O2 = 2.230D+17	H2 = 4.460D+17				
H2O	= 9.198D+12	H2O2 = 7.022D+12	M = 6.700D+17				

Pressure (torr) 5.1220D+01 (*pressure of reaction mixture*)

Conjugate functions of species:

YH	= -4.234D-02	YO = 8.717D-01	YOH = -4.324D-02				
----	--------------	----------------	------------------	--	--	--	--

Table 9.2. (Continued)

YHO2	= -4.268D-02	YO2 = -1.636D-06	YH2 = 8.173D-07				
YH2O =	3.950D-08	YH2O2 = 4.241D-05	YM = 3.043D-10				
Reaction conjugate functions: (<i>values of individual steps</i>)							
1...	-5.613D-03	2...	5.613D-03	3...	5.825D-05		
4...	-5.825D-05	5...	5.650D-02	6...	-5.650D-02		
7...	-6.211D-02	8...	6.211D-02	9...	-2.169D-05		
10...	2.169D-05	11...	6.217D-02	12...	-6.217D-02		
13...	5.494D-03	14...	-5.494D-03	15...	-1.131D-01		
16...	1.131D-01	17...	5.552D-03	18...	-5.552D-03		
19...	-9.480D-05	20...	9.480D-05	21...	3.375D-05		
22...	-3.375D-05	23...	5.540D-03	24...	-5.540D-03		
25...	-5.656D-02	26...	5.656D-02	27...	-2.450D-05		
28...	2.450D-05	29...	-6.213D-02	30...	6.213D-02		
31...	-6.105D-05	32...	6.105D-05	33...	-5.574D-03		

34...	5.574D-03	35...	-5.611D-03				
-------	-----------	-------	------------	--	--	--	--

-.62370E+10 (*Hamiltonian of reaction system*)

Weight functions: (value contributions of individual steps)

1... -1.075D-06	2... 2.509D-09	3... 9.884D-04					
4... -1.819D-09	5... 4.987D-01	6... -1.754D-05					
7... -4.993D-01	8... 1.056D-06	9... -2.830D-04					
10... 9.736D-16	11... 8.295D-07	12... -4.945D-07					
13... 5.590D-06	14... -1.908D-20	15... -1.365D-07					
16... 1.413D-23	17... 1.081D-07	18... -6.841D-28					
19... -9.207D-08	20... 2.458D-22	21... 3.413D-08					
22... -2.038D-19	23... 4.875D-09	24... -1.954D-09					
25... -1.887D-04	26... 6.304D-24	27... -1.984D-06					
28... 3.214D-04	29... -2.073D-04	30... 4.086D-14					
31... -7.820D-06	32... 3.401D-30	33... -7.814D-21					
34... 1.042D-15	35... -5.021D-06						

Elementary rates: (rates of individual steps, part. $cm^3 s^{-1}$)

1... 9.536D+10	2... 2.226D+08	3... 8.450D+15					
4... 1.555D+10	5... 4.396D+15	6... 1.546D+11					
7... 4.003D+15	8... 8.470D+09	9... 6.496D+15					
10... 2.235D+04	11... 6.645D+09	12... 3.961D+09					
13... 5.067D+11	14... 1.730D-03	15... 6.008D+08					
16... 6.221D-08	17... 9.695D+09	18... 6.136D-11					
19... 4.837D+11	20... 1.291D-03	21... 5.036D+11					
22... 3.006D+00	23... 4.382D+08	24... 1.757D+08					
25... 1.661D+12	26... 5.551D-08	27... 4.032D+13					
28... 6.533D+15	29... 1.661D+12	30... 3.275D+02					
34... 9.310D+01	35... 4.457D+11						

Below the computed dynamics for *value* contributions of main steps for the reaction of hydrogen with oxygen is presented.

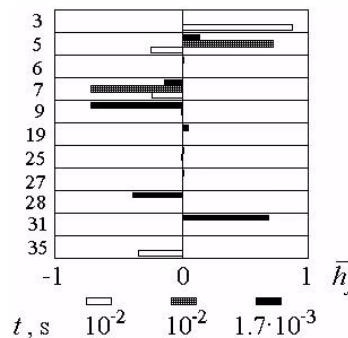


Figure 9.4. *Value* contributions of kinetically significant steps vs. time for the reaction of hydrogen with oxygen.

Thus, taking into consideration the illustrative examples in the present and previous chapters it may be concluded that the VALKIN software successfully solves many topical kinetic problems. Supplementing it with new subprograms, the scope of solved problems may be broadened over time and application of the *value* approach may be extended to other scientific fields.

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SUMMARY

This book is based on the idea that special methods are required to identify the role of species and individual steps in the progress of chemical processes as a whole, aimed at an in-depth understanding of the kinetic model, and the mechanism of complex (multistep) reactions, filling it with chemical content. This simultaneously expands the information field for planning new experiments aimed at updating the kinetic model for a multistep chemical reaction.

We believe that the objective quantitative interpretation of the kinetics, the time evolution of a chemical reaction, has to be in harmony with generally accepted approaches for the description of system dynamics. In accordance with this intention, we used the method of the *Hamiltonian systematization of kinetic models of reaction systems*. At the same time, the physical-chemical, kinetic comprehension of initial mathematical characteristics enabled to come to new systemic concepts in chemical kinetics, such as the *value* contributions of species and individual steps, specifying their kinetic significance in multistep processes.

The offered method by calculation of roles for species and individual steps of complex chemical reactions with consideration for the selected target characteristics is sufficiently comprehensive and harmonized with computing numerical methods. And we think that the information obtained is illustrative and physically and chemically easy to interpret.

The value discrimination of individual steps and species enables reducing the initial “redundant” kinetic models of reaction systems. By that one can succeed in the identification of the base (minimum) reaction mechanism that forms the basis of chemical transformation.

Value ranking of individual steps in the reaction kinetic model appears to be quite useful purposefully to influence chemical reactions (see Chapters 4, 6). Therewith, this problem attaches deeper meaning rather than the usually adopted optimal control of chemical process.

In this book we also addressed such an important issue of theoretical chemistry as the reactivity of species of multistep chemical reactions. A procedure was offered to identify the molecular structure of efficient reaction stimulators (the catalyst, initiator, promoter) and inhibitors. For this purpose the rate constants of individual steps involving the initial forms and their intermediate products were expressed through reaction indices, characterizing the initial molecule of a stimulator or inhibitor. *Considering the reactivity indices as parameters for controlling the chemical reaction system we succeeded in the identification of molecular design for the most efficient stimulator or inhibitor of a complex reaction.*

In Chapter 4 the opportunities on the application of the *value* concept, empirically to control complex chemical processes are discussed. At that the “selection” of key factors for

the influence was carried out among the pre-selected cause-and-effect relations between the species of chemical reactions.

We believe that versatility of the *value* analysis method of kinetic models and appropriate functional parameters is confirmed once more by its applicability to detailed studied chain processes (Chapter 5). We tried to demonstrate that parametric consequences of the offered approach, the *values* of species and individual steps supplement harmonically a number of underlying ideas of chain reactions, such as the average chain length, the self-acceleration factor, the constituent chain length, etc. (readers may judge how much we succeeded).

As shown in Chapters 5 and 8 the *value* method is also quite productive when discussing such an important issue as the identification and investigation of critical phenomena in chemical reactions. It enables to label the limits of fundamentally different regimes of reactions in chemically self-organizing oscillation systems.

Demonstrating the capabilities of the *value* analysis of reaction systems we applied to experimental data, mainly proceeding from private interests in chemical kinetics, although we think that its application fields may be considerably wider.

Investigations of inhibited reactions ultimately are intended to give recommendations for the selection of efficient inhibitors, as well as to define the most favorable conditions for these reactions and exploited materials. It is believed that here we succeeded in outlining certain solutions to the problem of *the nonempirical selection of the efficient antioxidant, based on the kinetic model of the inhibited chain reaction* - topical for the theory and application of oxidation processes.

Namely by the example of the inhibited oxidation of organic substances by oxygen, we tested our numerical method for the assessment and improvement of the prognostic capability of the kinetic model for multistep chemical reactions (see Chapters 4 and 7).

In closing we would like to note that investigating the kinetics of chemical reactions by the *value* method may supplement harmoniously the traditional approaches that were covered partially in this book. We think that combination of several methods to identify the adequate mechanism for a multistep chemical reaction and predicting its behavior will be very useful. Therefore, we hope that experts in the field of chemical kinetics will supplement the arsenal of the tools used by our method. In this case, our set objective would be achieved to a great extent.

GLOSSARY OF SYMBOLS

a	kinetic factor of chain propagation
a_i	kinetic parameter of species chemical transformation in the reaction flow graph
A	pre-exponential factor in the Arrhenius equation for the reaction constant $k=A\exp(-E/RT)$
$[A]$	concentration of chemical species A
A_{In}	activity of inhibitor
b_i	<i>value</i> contribution of the i -th species
c	kinetic factor of the intermediate product convesion in a degenerate branching-chain reaction
c_i	concentration of the i -th reaction species
c_f	concentration of a reaction species at the final time moment t_f
c_v	specific heat capacity
D	determinant
D	electron structure parameter for the reaction activator and inhibitor
D_i	addition to the determinant, characteristic for chain carrier i
D_{OH}	dissociation energy of O-H bond in the phenol's molecule, kJ/mol
e	yield of radical at initiation
E	activation energy of reaction, kJ/mol
F	output parameter of reaction
f	kinetic factor of chain-branching stage
f	kinetic factor of chain carrier formation from intermediate molecular substance
$f_i = dc_i/dt$	rate-of-production of the i -th species of a reaction system
$f_i = \mu_i / \mu_I$	normalizing factor
f_{In}	molar fraction of inhibitor in reaction mixture
g	kinetic factor of chain breaking
$G_i(t)$	<i>value</i> of the i -th individual step
$G_i^*(t)$	<i>value</i> of the i -th step in the reaction optimal controlling mode
$h_i(t)$	<i>value</i> contribution of the i -th individual step
$\bar{h}_i(t)$	reduced <i>value</i> contribution of the i -th individual step
$h_i^*(t)$	<i>value</i> contribution of the i -th step in the reaction optimal controlling mode

$h\nu$	energy of light quantum of frequency ν
H	Hamiltonian
ΔH^0	standard enthalpy change of a chemical reaction, kJ/mol
I	initiator
$I(t)$	target function or functional
In^\bullet	free radical formed by inhibitor
In, InH	inhibitor
$[\text{In}]_{\text{cr}}, [\text{InH}]_{\text{cr}}$	critical concentration of inhibitor
k_i	rate constant for the i -th reaction
$k_{\text{prop}} \& k_t$	rate constants for chain propagation and the breaking
k_{In}	rate constant of a reaction between chain carrier and inhibitor
K	conversion of the initial substance
m	stoichiometric factor of inhibition
$ M_i^j $	minor of determinant
n	concentration of chain carrier
N	total concentration of chain carriers
P	pressure of gaseous mixture
P_{In}, P_0	pressure of gaseous mixture matching explosion limit with and without inhibitor
r	rate of reaction
r_i	rate of the i -th individual step of a chemical reaction
$r_i^0, r_{\text{prop}} \& r_t$	rates of chain initiation, propagation and breaking
R	gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
S_{ij}	sensitivity of the concentration of the i -th species to the rate constant of the j -th individual step
S	selectivity of reaction
S_d	differential selectivity of reaction
t	time
$t^0 \text{C}$	temperature
T	absolute temperature, K
T	kinetic energy, J
$u(t)$	control parameter
u_c	control, confining the variation range of phase variables
u^{cl}	$u(t)$ value matching the condition $\partial H / \partial u = 0$
u^{lm}	control, taking into account imposed restrictions on control parameters
U	potential energy, J
x_i	species of reaction system; phase variable
α	probability of chain propagation
β	probability of chain breaking
ε	infinitesimality parameter
μ_i	stoichiometric coefficient of a reaction
δ	probability of chain branching
η_i	output parameter of the reaction kinetic model

θ	average time during which chain carriers are generated from the intermediate nonradical substance
ν	average chain length
ν_b	average chain length of branching-chain reaction
ν_i^j	constituent chain length
ν_{In}	chain length of reaction with an inhibitor
ρ	coefficient in the Hammet equation $\log(k/k_0) = \rho\sigma$
ρ	density of a reaction system
σ	Hammet function
τ_{ip}	induction period of a reaction
τ_{ch}	average chain time
φ	self-acceleration factor of branching chain reaction $\varphi = f - g$, s^{-1}
φ_r	yield of reaction
Φ_i	fitting function
ψ_i	conjugate function signifying the <i>value</i> of the <i>i</i> -th reaction species

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