Numerical Revelation of Kinetic Significance for Steps and Species in Complex Chemical Reaction Mechanisms by Hamiltonian Systematization Method

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Abstract. The method of numerical calculation of kinetic significance (value magnitude) of the individual steps is suggested by means of Hamiltonian systematization multistep chemical reaction model. The given computation method is displayed on the Chapman analyse model for ozone kinetics, as well as a tool of reduction model of formaldehyde oxidation reaction in the presence of carbon (II) oxide.

1 Introduction

The key question for mathematical simulation of complex (multistep) chemical reaction systems is to reveal the kinetic significance of steps and species in these reactions. This is connected with the solution of the following important tasks.

- to reveal the chemical basis of the multistep reaction - the role of molecular chemical conversion of species in the reaction system;
- to reduce the kinetic model of chemical reaction systems with revelation of the basic mechanism;
- to find ways for oriented effecting on multistep chemical reactions and their optimal control;
- to plan the experiment.

The objective of the present report is the development of a new universal method to have the steps and the species included in the chemical reaction kinetic model be numerically estimated.

2 Results

2.1 Characteristic of the Role of Individual Reaction Steps and Species via Value Magnitudes

A uniform chemical system at isothermal conditions may be presented in space as a set of usual differential kinetic equations:

$$\frac{dc_i}{dt} = f_i(k, c) \quad (1)$$

where $c(t)$ is the m -vector of species concentrations of $c(t_0) = c^0$, and k - the n - vector of rate constants.

Vector f involves a linear combination of step rates v_j which are presented in a form

$$v_j = k_j \prod_{l=1}^m c_e^{a_{je}} \quad (2)$$

where $a_{je} \geq 0$ and $\sum_{l=1}^m a_{je} \leq 3$.

The kinetic significance of reaction steps and species included in the reaction mechanism was determined using the approach of value magnitudes we have introduced before [1-3].

The value of G_j step is determined as the relation of response by a chosen characteristic magnitude of the reaction system, at any t moment of time, to perturbation of j reaction step rate at the t_0 moment of time:

$$G_j(t) = \frac{\partial F[v_1(t), \dots, v_n(t)]}{\partial v_j} \Big|_{v_j=v_j(t_0)}, \quad j=1, 2, \dots, n, \quad (3)$$

where $F(t)$ is the dynamic parameter of integral behavior; this parameter characterizes the chosen output value of reaction, e.g. the concentration of species, the yield of purposeful products, the reaction retardation period, etc.

Analogous, the value of a reaction system species is determined as the relation of output value (F) response, at a t moment of time, to perturbation of species concentration change rate at the t_0 moment of time:

$$\psi_i(t) = \frac{\partial F[f_1(t), \dots, f_m(t)]}{\partial f_i} \Big|_{f_i=f_i(t_0)}, \quad i=1, 2, \dots, m \quad (4)$$

where $f_i(t) = dc_i(t)/dt$ is the rate of concentration change for an i -th component.

It follows from (3) and (4) that the value of a i -th step equals to the difference of value between the species formed and participating in this reaction step:

$$G_j(t) = \sum_{i=1}^m \psi_i(t) \frac{\partial f_i}{\partial v_j} = \sum_p a_{jp} \psi_{jp}(t) - \sum_l a_{jl} \psi_{jl}(t) \quad (5)$$

where a_{jp} , a_{jl} are stoichiometric coefficients of the j -th elementary step, " p ", " l " - indexes relating, respectively, to products and to initial substances that step. Value contributions by h_j reaction steps and b_i species are determined taking into account the reaction steps rates and the rates of species accumulation:

$$h_j(t) = v_j(t)G_j(t) \quad \text{and} \quad b_i(t) = f_i(t)\psi_i(t) \quad (6)$$

2.2 Account of Value Parameters

The approach of Hamiltonian systematization for dynamic systems was used to calculate the value parameters.

Let the chosen property or the purpose functional be represented in an integral form:

$$I(t) = \int_{t_0}^t F(t) dt \quad (7)$$

For example, if it is aimed to reveal the role of reaction individual steps and species in the dynamics of change in concentration of the i -th species or several species, then the functionals, respectively, will be:

$$I_i(t) = c_i(t) = \int_{t_0}^t f_i(t) dt \quad I(t) = \sum_{i=1}^r c_i(t) = \sum_{i=1}^r \int_{t_0}^t f_i(t) dt \quad (8)$$

r - is the number of chosen species in reaction.

Rewriting equation (4) in an integral form

$$F = \sum_{i=1}^m \psi_i f_i + \text{const}, \quad (9)$$

and denoting

$$H = -F + \sum_{i=1}^m \psi_i f_i, \quad H = \text{const}, \quad (10)$$

correspondingly

$$\frac{dH}{dt} = \sum_i \left(\frac{\partial H}{\partial c_i} \frac{dc_i}{dt} + \frac{\partial H}{\partial \psi_i} \frac{d\psi_i}{dt} \right) = 0 \quad (11)$$

As in regard to (9) the system of equations might be represented in a form

$$\frac{dc_i}{dt} = \frac{\partial H}{\partial \psi_i} = f_i \quad i = 1, 2, \dots, m \quad (12)$$

then proceeding from (11)

$$\frac{dH}{dt} = \sum_i \left(\frac{\partial H}{\partial c_i} + \frac{d\psi_i}{dt} \right) \frac{dc_i}{dt} = 0, \quad (13)$$

Proceeding from (13) for an arbitrary $dc_i(t)/dt$ it follows that

$$\frac{d\psi_i}{dt} = - \frac{\partial H}{\partial c_i} \quad (14)$$

Thus it follows from equations (10), (12) and (14) that H is the Hamiltonian of the system. Values of components ψ_i and then, in compliance with (5) and (6) the value contributions of species and reaction steps are accounted by solving the system of conjugated equations (14) jointly with the kinetic equation (12). It must be mentioned that value magnitudes acquired by the present method are easy interpretable. In order to explain it from the point of view of physical meaning, the equation (10) is to be represented as

$$F = -H + \sum_{j=1}^n h_j = -H + \sum_{i=1}^m b_i \quad (15)$$

It follows from equation (15) that value contributions of h_j steps and those of the b_i species characterize their relative contribution into the chosen output parameter F for a multistep reaction, with an accuracy up to a constant.

Initial values of $\psi_i(t_0)$ required for the simulation of value parameters are determined by (4).

Thus, the procedure of accounting the value parameters, which forms the basis of the computer program VALKIN, is inferred to the following steps:

- setting up a system of kinetic equations (1);
- formal representation of the purpose functional for a multistep reaction (equation (7)) and the respective Hamiltonian of the system (equation (10));
- setting up a system of differential equations for $\psi_i(t_0)$ (values) - conjugated concentrations of species, in accordance with equation (14);
- estimation of conjugated function $\psi_i(t_0)$ values for the zero moment of time, proceeding from the purpose functional;

- e) computation of $\psi_i(t)$ dynamics by simultaneous solving the system of kinetic equations (1) and the system differential equations for conjugated functions (14);
- f) computation of dynamics for steps values, value contributions of individual reaction steps and species, according to equations (5) and (6), respectively.

3 Illustrative Examples

3.1 Ozone Kinetics

Chapman mechanism relating to the kinetics of atmosphere ozone conversion presented in Table 1 has been used as an illustrative example. This choice is conditioned by the fact that this example is assumed to be considered as a test model for new methods; other different methods of model analysis, in particular the method of sensitivity analysis were tested considering this example [4,6].

Mathematical program VALKIN that we have developed was used for numerical computation of reaction species concentration time profiles as well as reaction steps relative contributions. In this program the systems of differential equations are solved by the program ROW-4A [7].

The initial concentrations expressed in terms of number of particles to centimeter in cube, are the following: $[O]_0 = 10^6$, $[O_3]_0 = 10^{12}$ and $[O_2]_0 = 3,7 \cdot 10^6$.

At the first step one has to set up a system of kinetic equations (1) in accordance with the model represented in table 1.

For the revelation of stage contributions the purpose functional (8) is to be represented as:

$$I(t) = [O_3]_t = \int_{t_0}^t f_{O_3} dt \quad (16)$$

Here f_{O_3} - is the rate of change in ozone concentration.

The respective Hamiltonian, in compliance with (10), will be reduced to the following form

$$H = -f_{O_3} + \psi_O f_O + \psi_{O_3} f_{O_3} + \psi_{O_2} f_{O_2} \quad (17)$$

Then taking into account this form of Hamiltonian (17) a system of conjugated equation ψ_i (14) is to be set up.

The dynamics of ψ_O , ψ_{O_3} , ψ_{O_2} magnitudes was determined solving the system of differential equations (1) and (14). In accordance with the purpose functional (16) the initial values for ψ_O , ψ_{O_3} and ψ_{O_2} equal respectively $t_0: 0, 1, 0$. Based on values obtained for conjugate functions, according to equations (5) and (6), time dependencies of reaction (see Table 1) contributions were computed.

$$h_1 = (\psi_{O_3} - \psi_O - \psi_{O_2})v_1, \quad h_2 = (2\psi_{O_2} - \psi_O - \psi_{O_3})v_2$$

$$h_3 = (2\psi_O - \psi_{O_2})v_3, \quad h_4 = (\psi_O + \psi_{O_2} - \psi_{O_3})v_4$$

The results from value approach sufficiently enough coincide with the ones obtained by T. Hwang [4] by the analysis of ozone concentration sensitivity to variations of step rate constants. Though in general, in case of more complex reaction mechanisms, data from value approach could differ as well. This assertion is associated with the fact that in the case of reaction system response to step rate variation the role of steps is revealed to a more extent than when only the rate constant of that step is varied.

Table 1. Model of ozone kinetics. Time dependencies of steps relative value contributions ($\bar{h}_j$)

Reactions	Rate constant, (mole,sec,dm ³)	N	Value contribution of steps, $\bar{h}_j$		
			-1	0	1
$O_3 \rightarrow O + O_2$	2.50×10^{-4}	1			
$O_2 \rightarrow 2O$	5.00×10^{-11}	2			
$O + O_3 \rightarrow 2O_2$	4.66×10^{-16}	3			
$O + O_2 \rightarrow O_3$	1.63×10^{-16}	4			

Time, sec - $2 \cdot 10^{-2}$ - $3 \cdot 10^6$ - 10^7 - $5 \cdot 10^7$

3.2 The Reduction of the Reaction Mechanism of Gas Phase Chain Reaction of Phormaldehyde Oxidation in the Presence of Carbon (II) Oxide

The conscious choise of this object is conditioned by the fact that it turned out to be very useful approbation of reaction kinetic models reduction methods based on the method of sensitivity analysis [5,8,9].

Both the dominant and non-essential steps of reaction mechanism, shown in Table 3, were defined in work [5], on the bases of the isolated massive of the given species concentration sensitivity in accordance with the reaction step rate constant speech $5 \cdot 10^{-3}$ sec. for reaction time. Further, the use of a more systematic analyze method of the given sensitivity of concentration and of the accumulation rate of the species to the variations of step rate constant (the method of principal component analysis) succeeded in ranging the roles of reaction mechanism individual step of phormaldehyde oxidation in the presence of carbon(II) oxide. In these works the minimal mechanism reaction consists of 13 steps, at the average with an accuracy up to 2% giving the same results (the reaction time is $5 \cdot 10^{-3}$ sec.) as the initial kinetic model consisted of 25 steps (see Table 2).

Table 2. The Reaction Mechanism of Gas Phase Chain Reaction of Phormaldehyde Oxidation in the Presence of Carbon(II) Oxide

№	Reactions	Rate Constant
1.	$HC^{\bullet}O + O_2 \rightarrow HO_2^{\bullet} + CO$	$1 \cdot 10^{-13}$
2.	$HO_2^{\bullet} + CH_2O \rightarrow H_2O_2 + HC^{\bullet}O$	$5.7 \cdot 10^{-14}$
3.	$H_2O_2 + M \rightarrow 2HO^{\bullet} + M$	$6.66 \cdot 10^{-18}$
4.	$HO^{\bullet} + CH_2O \rightarrow H_2O + HC^{\bullet}O$	$1.6 \cdot 10^{-10}$
5.	$HO^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet}$	$5.1 \cdot 10^{-12}$
6.	$H_2O_2 \longrightarrow molec.products$	$1.05 \cdot 10^{+2}$
7.	$HO_2^{\bullet} \longrightarrow molec.products$	10.5
8.	$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2$	$3 \cdot 10^{-12}$
9.	$HO^{\bullet} + CO \rightarrow CO_2 + H^{\bullet}$	$3.3 \cdot 10^{-13}$
10.	$HO_2^{\bullet} + CO \rightarrow CO_2 + HO^{\bullet}$	$1.2 \cdot 10^{-15}$
11.	$H^{\bullet} + CH_2O \rightarrow H_2 + HC^{\bullet}O$	$2.7 \cdot 10^{-12}$
12.	$H^{\bullet} + O_2 \rightarrow HO^{\bullet} + \cdot O^{\bullet}$	$5.51 \cdot 10^{-14}$
13.	$H^{\bullet} + O_2 + M \rightarrow HO_2^{\bullet} + M$	$1 \cdot 10^{-32}$
14.	$HO_2^{\bullet} + M \rightarrow H^{\bullet} + O_2 + M$	$4.7 \cdot 10^{-19}$
15.	$\cdot O^{\bullet} + H_2 \rightarrow HO^{\bullet} + H^{\bullet}$	$3.02 \cdot 10^{-13}$
16.	$\cdot O^{\bullet} + CH_2O \rightarrow HO^{\bullet} + HC^{\bullet}O$	$1 \cdot 10^{-10}$
17.	$H^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2$	$1.3 \cdot 10^{-12}$
18.	$H^{\bullet} + H_2O_2 \rightarrow H_2O + HO^{\bullet}$	$5.9 \cdot 10^{-12}$
19.	$\cdot O^{\bullet} + H_2O_2 \rightarrow HO^{\bullet} + HO_2^{\bullet}$	$1 \cdot 10^{-13}$
20.	$HC^{\bullet}O \rightarrow H^{\bullet} + CO$	$4.6 \cdot 10^{-12}$
21.	$HO^{\bullet} + H_2 \rightarrow H_2O + H^{\bullet}$	$1 \cdot 10^{-11}$
22.	$CH_2O + O_2 \rightarrow HC^{\bullet}O + HO_2^{\bullet}$	$2.9 \cdot 10^{-20}$
23.	$H^{\bullet} + HO_2^{\bullet} \rightarrow 2HO^{\bullet}$	$5 \cdot 10^{-12}$
24.	$H^{\bullet} + HO_2^{\bullet} \rightarrow H_2O + \cdot O^{\bullet}$	$5 \cdot 10^{-11}$
25.	$H^{\bullet} + HO_2^{\bullet} \rightarrow H_2 + O_2$	$4.5 \cdot 10^{-11}$

Comments: The significance of the rate constant of the reaction is reduced to units: the number of the particles, cm, second, T=679 °C. The initial concentrations are

$[CH_2O]_0 = 6.77 \cdot 10^{16}$, $[O_2]_0 = 1.27 \cdot 10^{18}$, $[CO]_0 = 2.83 \cdot 10^{18}$ and $[M]_0 = 7.09 \cdot 10^{18} \text{ cm}^{-3}$.
 Now, let the stages of value analysis of kinetic model of formaldehyde oxidation in the presence of carbon (II) oxide be represented in a scheme. To begin with, let's single out the purpose functional characterizing the concentration change of the initial things: - formaldehyde, carbon oxide (II) and oxygen

$$I(t) = \Delta[CH_2O]_t + \Delta[CO]_t + \Delta[O_2]_t = - \int_0^t [f_{CH_2O} + f_{co} + f_{O_2}] dt \quad (18)$$

The system of the differential equation (12) and (13) is solved under the following initial significances of ψ_i . From the purpose functional (18) we have, that $\psi_{CH_2O}(0) = \psi_{CO}(0) = \psi_{O_2}(0) = -1$.

For other species ψ_i of the reaction during the initial moment of time the significance is equal to zero. Table 3 shows the calculated value contributions of the reaction steps, where the absolute significance is reduced gradually from 10^{-5} sec to $3 \cdot 10^{-3} \text{ sec}$. (conversion CH_2O 1.23%).

Table 3. The Comparison of the Step Numbers Being Arranged in the Reduction of their Kinetic Significance, Acquired by Different Methods, as well the Base (Minimal) Mechanism of the Reaction

Analyses Methods, Base model	Step Numbers															
Value Analysis	1	2	10	4	3	9	13	12	11	22	16	8	14	6	25	18
Sensitivity Analysis[3]	10	22	3	2	9	4	8	12	11	1	-	-	-	-	-	-
Principal Component Analysis[7]	22	10	4	9	2	16	12	11	1	13	14	3	6	7	24	8
Base Minimal Model of the Reaction [7,8]	1	2	3	4	6	8	9	10	11	12	13	16	22	-	-	-

Analyzing the findings from Table 3, it's obvious that the value contribution of the absolute magnitude the first 14 steps include the base mechanism of the reaction. The relative contributions of the reaction, not being included in the reaction mechanism, are only a few under the reaction time considered. It is worth mentioning that the individual step (14), being out of the base mechanism [7,8] occupies only the 13th

place in the isolated range. The base mechanism, consisted of 14 steps, including the step (14), describes the time profile of hydrogen atom concentration, which is deflected from the calculation of the initial model by 4%, and the isolated base model of the reaction in [7,8] consisted of 13 steps is deflected by 2,7%. However, for all species and especially for oxygen atoms, during the reaction time (from 10^{-5} sec. to $3 \cdot 10^{-3}$ sec.) this model is much less deflected from the calculation made by the use of initial models (25 steps). To compare, we can pay attention on the fact, that in (17) the first 16 steps of the analogous rate were taken into consideration for the isolated base mechanism of the reaction. The individual step 8, being included in the base mechanism, according to the calculation, has little significance and occupies the 16th place in the range. Whereas, the step 14, being isolated as ponderable enough for the reaction, isn't included in the base mechanism.

Now let's focus our attention on the role of the decrease order of the step. The decrease order of kinetic significance of the reaction steps, isolated by value methods, generally coincides with literature data, being defined by sensitivity analyze method [5,8,9]. Some of the observed differences apparently are connected with the difference of the value characteristics and parameters of sensitivity, which define the kinetic significance of the step [1-3]. Here the essential role can take the very circumstance, which by the value analysis of kinetic model reaction is distinctly selected as an index of the reaction quality: a purpose functional on which wholly depends the kinetic significance of the reaction step.

So, the examples of kinetic model of formaldehyde oxidation in the presence of carbon (II) oxide makes it quite possible to be completely convinced that the value analysis is a reliable mathematical tools of reduction mechanisms which reveals the base kinetic model of chemical conversion.

Thus we have worked out a new numerical method and a relevant computer program VALKIN for the analysis of chemical reaction models, which widen the scope of means for specialists in the field of chemical kinetics and engineering.

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