Preprints of the 19th World Congress
The International Federation of Automatic Control
Cape Town, South Africa. August 24-29, 2014

The Network Operator Method for Identifications of Chemical Reactions

A.I. Diveev*, I.M. Gubaidullin, E.A. Sofronova*****

** Institution of Russian Academy of Sciences Dorodnicyn Computing Centre of RAS*
Moscow, Russia (Tel: +7-905-711-4427; e-mail: aidiveev@mail.ru)
*** Institution of Petrochemistry and Catalysis of RAS*
Ufa, Russia (Tel: +7-917-340-5022; e-mail: irekmars@mail.ru)
**** Peoples' Friendship University of Russia,*
Moscow, Russia, (Tel:+7-915-414-3700; e-mail: sofronova_ea@mail.ru)

Abstract: A problem of identification of mathematical model of chemical reaction is considered. Mathematical model in the form of ODE is obtained from the experimental data of concentrations changes during the reaction process. To solve the identification problem we use a numerical network operator method that allows finding structure and parameters of mathematical expression presented as an integer matrix. The network operator method uses evolutionary search algorithms. A numerical example of identification for the chemical generation singlet oxygen reaction is given.

1. INTRODUCTION

For more than 70 years, researchers in several areas of science have been intrigued by the physical and chemical properties of the lowest excited states of molecular oxygen. With two singlet states lying close above its triplet ground state, the O2 molecule possesses a very unique configuration, which gives rise to a very rich and easily accessible chemistry, and also to a number of important photophysical interactions. In particular, photosensitized reactions of the first excited state, 1O2, play a key role in many natural photochemical and photobiological processes, such as photodegradation and aging processes including even photocarcinogenesis. Reactions of 1O2 are associated with significant applications in several fields, including organic synthesis, bleaching processes, and, most importantly, the photodynamic therapy of cancer, which has now obtained regulatory approval in most countries for the treatment of several types of tumors (Schweitzer, Schmidt, 2003).

Mathematical modeling of atomic-molecular and nanolevels is necessary to understand the mechanism of the process, to obtain the correct (usually nonlinear) dependence of the rate of chemical transformations of the reaction mixture composition and properties of the reaction surface, temperature and other process parameters. The result of these studies is the kinetic model of the reaction (Boreskov and Slin'ko, 1961, 1964). The kinetic model provides the necessary theoretical and practical information for the mathematical modeling of catalytic reactions, the reactor design and determine the optimal conditions of the industrial process (Kuchanov et al., 1991, Zyskin et al., 1981).

At present, the construction of kinetic models based on existing methods is the most time-consuming and lengthy stage of the study. Because of this during the development of the catalytic process is increased, the number of errors and the industry suffers significant economic loss (Wasserman, Murray, 1979). Therefore, the accuracy and efficiency of kinetic modeling is of great practical importance to shorten the research and development of new catalytic processes.

The development of kinetic models is done by solving inverse problem of physical chemistry. It deals with minimization of deviation between experimental data and calculated values. It requires multiple primal kinetic problems solving.

The main physic-chemical law which is used to simulate the chemical reactions is the law of mass action, which states that the speed of the elementary reaction is proportional to the product of the concentrations of the reacting molecules, was established in 1867 by the Norwegian mathematician K. Guldberg and chemist P. Waage.

Studying mechanisms of complex chemical reactions both physic-chemical and mathematical problems occur. Physic-chemical problems deal with measurement complexity of intermediate compounds that may initiate mathematical ambiguity of inverse problem solution for kinetic parameters determination.

Mathematical problem lies in the fact that certain conditions complex physical and chemical processes are not always described by the law of mass action. For example, sometimes in the kinetic equations the functional dependence of the Langmuir-Hinshelwood mechanism, taking into account the slowdown in certain stages of the chemical transformation is used (Slin'ko, et al., 1982, 1997). Plans are to search more adequate mathematical descriptions of chemical reactions; in this paper we consider a new approach to the establishment of the laws of chemical reaction rate dependence on the concentration of the participating agents.

To solve the problem of identification for the chemical reaction we use a method of network operator (Diveev, Sofronova, 2008, 2009, 2012, Diveev, 2012). This method allows presenting mathematical expressions in the form of integer matrices using a new data structure, a network

operator. Applying this method we can find structure and parameters of nonlinear mathematical model of reaction.

2. IDENTIFICATION OF CHEMICAL REACTION MODEL

Consider the identification of chemical reaction mathematical model.

The observed results of changing concentrations of substances that participate in reaction are given

$$\mathrm{X} = \left(\left(t_0, \mathbf{y}^0 \right), \ldots, \left(t_N, \mathbf{y}^N \right) \right), \quad (1)$$

where $\mathbf{y}^k$ is an observed vector of values of concentrations at moment t_i, $\mathbf{y}^k = \left[y_1^k \ \ldots \ y_m^k \right]^T$, $t_{k-1} < t_k$, $k = \overline{1,N}$,

$$y_j^k = \varphi_j(\mathbf{x}), \ k = \overline{1,N}, \ j = \overline{1,m}, \quad (2)$$

$\mathbf{x} = \left[x_1 \ \ldots \ x_n \right]^T$, x_i is a concentration of substance i, $\varphi_j(\mathbf{x})$ are known function, that describe the values of changing concentrations.

It is known that initially in the reaction participate $l < n$ substances. The rest $n - l$ substances are obtained as a result of reaction.

To describe changing concentrations in time we define the system of differential equations

$$\dot{\mathbf{x}} = \mathbf{f}\left(\mathbf{v}(x_1, \ldots, x_l) \right), \quad (3)$$

where

$$\mathbf{v}(x_1, \ldots, x_l) = \left[v_1\left(x_{i_1}, x_{j_1} \right) \ldots \ v_r\left(x_{i_r}, x_{j_r} \right) \right]^T,$$
$$1 \le i_1, j_1, \ldots, i_r, j_r \le l.$$

Functions $v_p\left(x_{i_p}, x_{j_p} \right)$ describe the law of concentrations x_{i_p} and x_{j_p} changes at interaction of substances i_p and j_p:

$$v_p = g\left(q_p, x_{i_p}, x_{j_p} \right), \ p = \overline{1,r}, \quad (4)$$

where q_p is unknown constant parameter, $p = \overline{1,r}$.

We suppose that the structure of function $g\left(q_p, x_{i_p}, x_{j_p} \right)$ and values of parameters q_p, $p = \overline{1,r}$, are unknown.

The constraints are given in the form of algebraic balance equations

$$\alpha_j(\mathbf{x}) = 0, \ j = \overline{1,M}. \quad (5)$$

It is necessary to find functions (4) and parameters q_p, $p = \overline{1,r}$, so that having solved the system of differential equations (3) for given initial values

$$x_1(0) = x_1^0, \ \ldots, \ x_l(0) = x_l^0, \ x_{l+1}(0) = 0, \ldots, x_n(0) = 0, \quad (6)$$

we could minimize the quality criterion

$$J = \sum_{j=1}^{m} \omega_j \sqrt{ \sum_{k=1}^{N} \left(y_j^k - \varphi(\mathbf{x}(t_k)) \right)^2 }, \quad (7)$$

where $\mathbf{x}(t_k)$ is a solution of (3) at moment t_k, and fulfils the balance equations (5)

$$\alpha_j(\mathbf{x}(t_k)) = 0, \ k = \overline{1,N}. \quad (8)$$

In most mathematical models interaction of substances (4) was presented by the law of K. Guldberg and P. Waage. According to this law velocities of interaction of substances are proportional to multiplication of their concentrations raised to the certain powers. In works (Slin'ko et al., 1997) using generalized models of chemical reactions the power of concentrations equals to one. To identify the model it was necessary to find only the values of parameters. In present work to identify the mathematical model we use a method of network operator.

3. METHOD OF NETWORK OPERATOR

To solve the problem of identification we use a method of network operator. Mathematical expressions are presented in the form of directed graphs. The structure of graph shows arguments of any function in the mathematical expression and the order of operations.

Network operators consist of the following constructive sets:
- set of variables

$$\mathrm{X} = (x_1, \ldots, x_N), \ x_i \in \mathrm{R}^1, \ i = \overline{1,N}; \quad (9)$$

- set of parameters

$$\mathrm{Q} = (q_1, \ldots, q_P), \ q_i \in \mathrm{R}^1, \ i = \overline{1,P}; \quad (10)$$

- unary operations set

$$\mathrm{O}_1 = (\rho_1(z) = z, \rho_2(z), \ldots, \rho_W(z)); \quad (11)$$

- binary operations set

$$\mathrm{O}_2 = (\chi_0(z', z''), \ldots, \chi_{V-1}(z', z'')). \quad (12)$$

The set of unary operations must include the identity operation, $\rho_1(z) = z$.

Binary operations are commutative

$$\chi_i(z', z'') = \chi_i(z'', z'), \ i = \overline{0,V-1}, \quad (13)$$

associative

$$\chi_i(z', \chi_i(z'', z''')) = \chi_i(\chi_i(z', z''), z'''), \ i = \overline{0,V-1}, \quad (14)$$

and have a unit element

$$\forall \chi_i(z',z'') \in \mathrm{O}_2,\ \exists e_i,\ \chi_i(e_i,z)=z,\ i=\overline{0,V-1}. \qquad (15)$$

Numeration of elements in set O_2 starts from zero, numeration of elements in set O_1 starts from one. Unit elements for these operations are zero and one respectively. When we present a network operator as a matrix zeros in positions for unary operations mean the absence of unary operations.

The network operator is a directed graph where each source node corresponds to parameter or variable, other nodes - to binary operations, edges – to unary operations, the results are kept in the sink nodes.

To present a network operator in the PC memory we use a network operator matrix (NOM)

$$\boldsymbol{\Psi} = \left[\psi_{i,j}\right],\ i,j=\overline{1,L}, \qquad (16)$$

where L is a number of nodes in a network operator.

NOM has the same structure as the adjacency matrix of the graph. We replace ones in the adjacency matrix by corresponding unary operations $\psi_{i,j}=k$, if the edge (i,j) corresponds to operation $\rho_k(z)$. The main diagonal elements contain indices of binary operations $\psi_{i,i}=m$, if the node i corresponds to binary operation $\chi_m(z',z'')$.

All nodes in the network operator should be numerated so that the index of the node where the edge comes out is less than the index of the node where this edge comes in $\forall(i,j)$ $i<j$. Thus the NOM is upper triangular, and we can calculate the result of mathematical expression.

Here we present the most commonly used unary and binary operations.

$$\mathrm{O}_1 = \Big\{\ \rho_1(z)=z,\ \rho_2(z)=z^2,\ \rho_3(z)=-z,$$

$$\rho_4(z)=\mathrm{sgn}(z)\sqrt{|z|},\ \rho_5(z)=z^{-1},\ \rho_6(z)=e^z,\ \rho_7(z)=\ln|z|,$$

$$\rho_8(z)=\frac{1-e^{-z}}{1+e^{-z}},\ \rho_9(z)=\begin{cases}1, & \text{if } z\ge 0\\ 0, & \text{otherwise}\end{cases},\ \rho_{10}(z)=\mathrm{sgn}(z),$$

$$\rho_{11}(z)=\cos(z),\ \rho_{12}(z)=\sin(z),\ \rho_{13}(z)=\arctan(z),$$

$$\rho_{14}(z)=z^3,\ \rho_{15}(z)=\sqrt[3]{z},\ \rho_{16}(z)=\begin{cases}z, & \text{if } |z|<1\\ \mathrm{sgn}(z), & \text{otherwise}\end{cases},$$

$$\rho_{17}(z)=\mathrm{sgn}(z)\ln(|z|+1),\ \rho_{18}(z)=\mathrm{sgn}(z)\left(e^{|z|}-1\right),$$

$$\rho_{19}(z)=\mathrm{sgn}(z)e^{-|z|},$$

$$\rho_{20}(z)=\begin{cases}1, & \text{if } z>\varepsilon\\ 0, & \text{if } z<0\\ 3z^2/\varepsilon^2-2z^3/\varepsilon^3, & \text{otherwise}\end{cases},$$

$$\rho_{21}(z)=\begin{cases}1, & \text{if } z>\varepsilon/2\\ -1, & \text{if } z<-\varepsilon/2\\ 3z/\varepsilon^2-4z^3/\varepsilon^3, & \text{otherwise}\end{cases},\ \rho_{22}(z)=e^{-|z|},$$

$$\rho_{23}(z)=z-z^3,\ \rho_{24}(z)=\frac{1}{1+e^{-z}}\Big\},$$

$$\mathrm{O}_2 = \big\{\chi_0(z',z'')=z'+z'',\ \chi_1(z',z'')=z'z'',$$
$$\chi_2(z',z'')=\max\{z',z''\},\ \chi_3(z',z'')=\min\{z',z''\},$$
$$\chi_4(z',z'')=z'+z''-z'z'',$$
$$\chi_5(z',z'')=\mathrm{sgn}(z'+z'')\sqrt{(z')^2+(z'')^2},$$
$$\chi_6(z',z'')=\mathrm{sgn}(z'+z'')(|z'|+|z''|),$$
$$\chi_7(z',z'')=\mathrm{sgn}(z'+z'')\max\{|z'|,|z''|\}\ \big\}.$$

All these binary operations are associative, commutative and have unit elements $e_0=0$, $e_1=1$, $e_2=-\varepsilon^{-1}$, $e_3=-\varepsilon^{-1}$, $e_4=0$, $e_5=0$, $e_6=0$, $e_7=0$.

Network operator matrix $\boldsymbol{\Psi}$ of dimension $L\times L$ contains sets of N variables, P parameters, W unary operations and V binary operations. NOM can present

$$K_O = V^{L-N-P}\prod_{j=N+P+1}^{L}\sum_{k=1}^{j-1}G(k)W^k, \qquad (17)$$

where

$$G(k)=\frac{(j-1)!}{(j-1-k)!k!}, \qquad (18)$$

different mathematical expressions.

Network operators which matrices are of the same dimension and have the same indices of the nodes for variables, parameters and outputs are called **alike network operators**.

Let $\Xi(L)$ be a set of alike network operators of dimension L. The cardinal of set $\Xi(L)$ is determined by (18). We search for solution over this set. The search is complicated by the fact that the elements of set have nonnumerical codes. Nonnumerical codes are the codes for which arithmetical operations of addition and multiplication are not performed.

To organize a directed search of optimal network operator we define a metrics on the set of alike network operators as a sum of differences between matrices

$$\delta(\boldsymbol{\Psi}^k,\boldsymbol{\Psi}^l)=\sum_{i=1}^{L}\sum_{j=1}^{L}\vartheta\left(\left|\Psi_{i,j}^k-\Psi_{i,j}^l\right|\right), \qquad (19)$$

where $\boldsymbol{\Psi}^k,\boldsymbol{\Psi}^l\in\Xi(L)$, $\boldsymbol{\Psi}^k=\left[\Psi_{i,j}^k\right]$, $\boldsymbol{\Psi}^l=\left[\Psi_{i,j}^l\right]$, $i,j=\overline{1,L}$, $\vartheta(A)$ is Heaviside function

$$\vartheta(A)=\begin{cases}1, \text{ if } A>0\\ 0 \text{ otherwise}\end{cases}.$$

If $\boldsymbol{\Psi}^k, \boldsymbol{\Psi}^l \in \Xi(L)$ and $\delta\left(\boldsymbol{\Psi}^k, \boldsymbol{\Psi}^l\right)=\Delta$, then we say that the distance between network operators $\boldsymbol{\Psi}^k$ and $\boldsymbol{\Psi}^l$ is equal to Δ.

Define Δ **-neighborhood of network operator** as a subset of network operators $\boldsymbol{\Omega}\left(\boldsymbol{\Psi}^i, \Delta\right) \subseteq \Xi(L)$ that are no more than Δ far from the network operator $\boldsymbol{\Psi}^i$,

$$\forall \boldsymbol{\Psi}^j \in \boldsymbol{\Omega}\left(\boldsymbol{\Psi}^i, \Delta\right),\ \delta\left(\boldsymbol{\Psi}^i, \boldsymbol{\Psi}^j\right) \le \Delta.$$

Let us have a function $f_0(\boldsymbol{\Psi})$ on the set $\Xi(L)$ of network operators. Then we consider that the function $f_0(\boldsymbol{\Psi})$ reaches its local minimum on the set of network operators, if $\exists \widetilde{\boldsymbol{\Psi}}$ that $\forall \boldsymbol{\Psi} \in \boldsymbol{\Omega}\left(\widetilde{\boldsymbol{\Psi}}, 1\right)$,

$$f_0(\boldsymbol{\Psi}) \ge f_0\left(\widetilde{\boldsymbol{\Psi}}\right).$$

Suppose $\mathbf{w}$ is variation operator or simply variation of network operator

$$\mathbf{w} \circ \boldsymbol{\Psi} \ne \boldsymbol{\Psi}. \tag{20}$$

A small variation of network operator is a variation that fulfills the condition

$$\delta(\mathbf{w} \circ \boldsymbol{\Psi}, \boldsymbol{\Psi}) = 1. \tag{21}$$

The condition of local minimum of function $f_0(\boldsymbol{\Psi})$ on the set $\boldsymbol{\Omega}(\boldsymbol{\Psi}, \Delta)$ is the following

$$f_0(\mathbf{w} \circ \boldsymbol{\Psi}) - f_0(\boldsymbol{\Psi}) \ge 0, \tag{22}$$

where $\mathbf{w} \circ \boldsymbol{\Psi} \in \boldsymbol{\Omega}(\boldsymbol{\Psi}, \Delta)$.

Small variations of network operator may differ from each other. For network operator small variations are:

0 – a replacement of unary operation,
1 – a replacement of binary operation,
2 – an addition of unary operation,
3 – a deletion of unary operation.

Operation 3 requires that the elements in columns and rows of network operator that are not source nodes cannot be equal to zero. To present variations we use a vector of four elements

$$\mathbf{w} = \left[w_1 \ \ w_2 \ \ w_3 \ \ w_4\right]^T, \tag{23}$$

where w_1 is a number of small variation, w_2 is a number of row, w_3 is a number of column, w_4 is a number of unary or binary operation.

To search for the optimal network operator $\widetilde{\boldsymbol{\Psi}}$ we use ordered sets of elementary variations

$$\mathrm{W}_i = \left(\mathbf{w}^{i,1}, \ldots, \mathbf{w}^{i,l}\right), \tag{24}$$

$$\mathrm{W}_i \circ \boldsymbol{\Psi} = \mathbf{w}^{i,l} \circ \ldots \circ \mathbf{w}^{i,1} \circ \boldsymbol{\Psi}. \tag{25}$$

The search algorithm of optimal mathematical expression has the following steps.

We start from the network operator $\boldsymbol{\Psi}^0$ that is supposed by the researcher to be close to the desired solution. This network operator is called a **basis network operator**.

Then we generate sets of variations $\mathrm{W}_i = \left(\mathbf{w}^{i,1}, \ldots, \mathbf{w}^{i,l}\right)$, $i = \overline{1, H}$, and calculate the values of goal function for each new network operator $f_0\left(\mathrm{W}_i \circ \boldsymbol{\Psi}^0\right)$.

If we find a network operator with a better value of goal function than the basis network operator then we replace the basis network operator with a new found one.

If $f_0\left(\mathrm{W}_i \circ \boldsymbol{\Psi}^0\right) < f_0\left(\boldsymbol{\Psi}^0\right)$, then $\boldsymbol{\Psi}^0 \leftarrow \mathrm{W}_i \circ \boldsymbol{\Psi}^0$.

The probability P_A of finding optimal network operator with the help of the algorithm proposed depends on the number H of generated sets of variations.

$$\lim_{H \to \infty} P_A = 1. \tag{26}$$

Any evolutionary algorithm can be applied to the search. In our research we use genetic algorithm where genetic operations are performed on the ordered sets of elementary variations (24).

4. AN EXAMPLE

As an example, consider the chemical reaction of singlet oxygen generation.

For many years singlet oxygen $^1O_2$ has been attracting the attention of researchers because of its essential role in the organic synthesis and biological processes (Wasserman, Murray, 1979). Equally important is the involvement of $^1O_2$ in the chemluminescent reactions (Kazakov *et al*., 2007). Previously, the reaction accompanied by the high-efficiency generation of $^1O_2$, namely the collapse dioxiranes (Adam *et al*., 1989) catalyzed by the series of anions ($Cl-$, $Br-$, $I-$, $OH-$, O_2-) (Adam *et al*., 2002) was found. The yield of singlet oxygen measured in this peroxide system by IR-CL method is high enough.

The data on the laws of this reaction will be useful for a better understanding of the processes of generation of excited states in the reactions of peroxides, as well as for understanding of factors affecting the stability of dioxiranes in solution. The high yield of $^1O_2$ can be considered a dioxirane-nucleophilic ion system as a promising one for the chemical lasers and organic synthesis.

The differential equation (3) describing the changes in the concentrations of substances in the study of the catalytic process generating $^1O_2$ based on the proposed scheme of

chemical transformations in (Ovchinnikov *et al*., 2010) are of the form

$$\dot{x}_1 = -v_1 - v_2 - v_3,$$

$$\dot{x}_2 = -v_1 + v_2,$$

$$\dot{x}_3 = v_1 - v_2 - v_3,$$

$$\dot{x}_4 = v_2,$$

$$\dot{x}_5 = v_2,$$

$$\dot{x}_6 = v_3,$$

$$\dot{x}_7 = v_3,$$

where

$$v_1 = g(q_1, x_1, x_2),$$

$$v_2 = g(q_2, x_1, x_3),$$

$$v_3 = g(q_3, x_1, x_3),$$

$g(q,a,b)$ is unknown function of three arguments, q_i are unknown values of constant parameters, $i = 1,2,3$.

For the system of differential equations we have the initial conditions: $x_1(0) = 0.881834215$, $x_2(0) = 0.118165785$, $x_i(0) = 0$, $i = \overline{3,7}$.

Balance equations (5) are

$$3x_1 + 3x_3 + 3x_5 + 3x_6 + 3x_7 = 3x_1(0),$$

$$6x_1 + 6x_3 + 6x_5 + 6x_6 + 6x_7 = 6x_1(0),$$

$$2x_1 + 2x_3 + 2x_4 + x_5 + 2x_6 + 2x_7 = 2x_1(0),$$

$$x_2 + x_3 + x_7 = x_2(0).$$

Let us consider an example of concentrations changing estimation by the value of intensity

$$y = \frac{x_1 x_2}{x_1(0) x_2(0)}.$$

In our research we tried to improve the law of K. Guldberg and P. Waage. The law stipulates that the velocity v_p of changing of concentrations of substances x_i and x_j in reaction p is proportional to multiplication of these substances concentrations raised to certain powers

$$v_p = q_p x_{i_p}^{\alpha} x_{j_p}^{\beta}.$$

It is usually assumed that $\alpha = 1$, $\beta = 1$ and parameters q_p are searched for.

We used this law as a basis solution and tried to find its presentation by method of network operator.

To solve the problem we used a method of network operator and evolutionary algorithm. The parameters of the variation genetic algorithm with multiple basis were: cardinal of initial set of possible solutions 512; number of generations 128; number of crossovers in one generation 256; number of variations in one solution 4; number of generations between epochs 16; number of elite solutions 12; probability of mutation 0.7; crossover parameter 0.4; number of bases 5.

Our approach is realized in the specific software NOP4C-I developed for the identification of control systems.

As a result we obtained the following network operator matrix

$$\mathbf{\Psi} = \begin{bmatrix} 0 & 0 & 0 & 23 & 5 & 0 & 0 & 0 \\ 0 & 0 & 0 & 23 & 14 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 23 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 23 & 0 & 3 \\ 0 & 0 & 0 & 0 & 0 & 1 & 23 & 3 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 15 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix},$$

which corresponds to the following mathematical expression

$$g(q_i,a,b) = \sqrt[3]{A - A^3 - \left(A - A^3\right)^3} - 2A + A^3 -$$

$$- q_i\left(a - a^3\right)\left(b - b^3\right) + \left(a - a^3\right)^3\left(b - b^3\right)^3 \frac{b^3}{a},$$

where

$$A = q_i\left(b^5 - a^2 b^4 - b^6 + a^2 b^6\right) - \frac{q_i}{a}\left(ab^2 - a^3 b^2 - ab^4 + a^3 b^4\right)^3.$$

For parameters q_i the values are: $q_1 = 26.09753$, $q_2 = 0.01590$, $q_3 = 314.67213$.

Obtained mathematical expression can be considered as correction of law proposed by K. Guldberg and P. Waage.

The plot of experimental and calculated values of the intensities obtained with the identified functions $g(q_i,a,b)$ is presented in Fig.1.

Plot on Fig. 1 shows high accuracy of obtained mathematical model of chemical reaction. The results of calculations may lead to certain correction of interaction law of substances proposed by K. Guldberg and P. Waage that concentrations of substances at their interaction are proportional to multiplication of polynomials from concentrations of each substance.

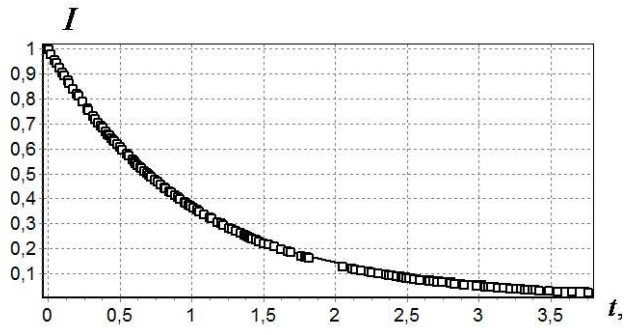

Fig. 1. The experimental and calculated values of the intensities at 283 K.

5. CONCLUSIONS

Application of method of network operator for the problem of chemical reaction model identification allowed obtaining mathematical model of substances interaction reaction. Comparison with experimental data proved high accuracy of obtained model which includes new mathematical expression that presents the law of substances interaction. This mathematical expression can be considered as correction of law proposed by K. Guldberg and P. Waage.

Further research is also expected to treat an array of data for temperatures 288K and 316K, and investigate obtained mathematical expression for these reactions.

6. ACKNOWLEDGMENTS

Work has been executed with support of Russian Fund of Basic Researches on the projects № 12-07-00324-a, № 13-08-00523-a.

REFERENCES

Adam, W., Curci, R. and Edwards, J.O. (1989). Dioxiranes: a new class of powerful oxidants. *Acc. Chem.* Res. **Vol. 22.** P. 205-211.

Adam, W., Kiefer, W., Schlucker, S., Saha-Muller, C., Kazakov, D.V., Kazakov, V.P. and Latypova, R.R. (2002). *Bioluminescence and Chemiluminescence: Progress and Current Applications* (Stanley, P.E., Kricka, L.J. (Ed).) Singapore: World Scientific Publishing, 2002. P.129

Boreskov, G.K., Slinko, M.G. (1961) Calcul des prosessus catalytiques dans les uacteurs industriels. *Chem. Eng. Sci.* **Vol. 14.** P. 259.

Boreskov, G.K. and Slinko, M.G. (1964). Exothermal Catalytic Process Simulation. *Third European Symposium on Chem. Reac. Engin.* Pergamon. Press.

Diveev, A.I. and Sofronova, E.A. (2008). Application of network operator method for synthesis of optimal structure and parameters of automatic control system. *Proceedings of 17-th IFAC World Congress,* Seoul, 05.07.2008 – 12.07.2008. P. 6106 – 6113.

Diveev, A.I. and Sofronova, E.A. (2009). Numerical method of network operator for multiobjective synthesis of optimal control system. *Proceedings of Seventh International Conference on Control and Automation (ICCA'09)* Christchurch, New Zealand, December 9-11, 2009. P. 701-708.

Diveev, A.I. (2012). A Numerical Method for Network Operator for Synthesis of a Control System with Uncertain Initial Values. *Journal of Computer and Systems Sciences International*, **Vol. 51**, No. 2, P. 228–243.

Diveev, A.I. and Sofronova, E.A. (2012). The Network Operator Method for Search of the Most Suitable Mathematical Equation. *Chapter in the book Bio-Inspired Computational Algorithms and Their Applications* (Shangce Gao (Ed)). Intech. Printed 2012. February, Croatia. P. 19-42.

Kazakov, D.V., Kazakov, V.P., Maistrenko, G.Ya., Mal'zev, D.V. and Schmidt, R. (2007). On the Effect of 1,4-Diazabicyclo [2.2.2] octane on the Singlet-Oxygen Dimol Emission: Chemical Generation of $\left(^1O_2\right)_2$ in Peroxide Reactions, *J. Phys. Chem.* 2007. **Vol. 111**. P. 4267-4273.

Kuchanov, S.I., Pugin, S.V. and Slin'ko, M.G. (1991). Mathematical modeling of copolymerization. *Matem. Mod.*, **Vol.3**, 5. P. 110–121.

Ovchinnikov, M.Yu., Khursan, S.L., Kazakov, D.V. and Adam, W. (2010). The Theoretical Trajectory for the Chloride-Ion-Induced Generation of Singlet Oxygen in the Decomposition of Dimethyldioxirane, *J. Photochem. Photobiol. A. Chem.* **Vol. 210**. P. 100-107.

Slin'ko, M.G. and Slin'ko, M.M. (1982). Auto-oscillations of the Rate of Heterogeneous Catalytic Reactions. *Kinetics and Catalysis*, **Vol. 23(6)**. P. 1208-1213.

Slin'ko M.G., Zelenyak, T.I., Akramov, T.A., Lavrent'ev, M.M. (Jn.) and Sheplev, V.S. (1997). Nonlinear dynamic of catalytic reactions and process (review). *Matem. Mod.*, **Vol. 9,**12. P. 87–109.

Schweitzer, C. and Schmidt, R. (2003). Physical Mechanisms of Generation and Deactivation of Singlet Oxygen. *Chemical Reviews*, **Vol. 103(5)**, P. 1685—1757.

Wasserman, H.H. and Murray, R.W. (1979). *Organic Chemistry: Singlet Oxygen.* N.Y.: Acad. Press, **Vol.40.**

Zyskin, A.G., Snagovskii, Yu.S. and Slin'ko, M.G. (1981). Studies of the dynamic properties of heterogeneous catalytic reactions in a closed adiabatic gradientless system over biographically inhomogeneous catalyst surface. *Reaction Kinetics and Catalysis Letters.* 31. X. 1981, **Vol. 17**, Issue 3-4. P. 263-267.