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APPLICATION OF DISCRETE STOCHASTIC MODELS TO DESCRIBE CHEMICAL KINETICS

ZASTOSOWANIE DYSKRETNYCH MODELII STOCHASTYCZNYCH DO MODELOWANIA KINETYKI CHEMICZNEJ

Abstract

The possibility of application of the theory of discrete Markov chains to model chemical reactions is examined in the paper. The physico-chemical approach of mathematical objects that describe the discrete Markov chain is discussed. Some of examples of modeling chemical reaction kinetics are presented.

Keywords: discrete Markov chain, chemical kinetics, simulation

Streszczenie

W artykule przedstawiono możliwości zastosowania teorii dyskretnych łańcuchów Markowa do modelowania kinetyki reakcji chemicznych. Omówione jest znaczenie fizyko-chemiczne obiektów matematycznych, które opisują dyskretny łańcuch Markowa. Przedstawiono wybrane przykłady modelowania kinetyki reakcji chemicznych.

Słowa kluczowe: dyskretny łańcuch Markowa, kinetyka chemiczna, modelowanie

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1. Introduction

During the last year the interest in application of the mathematical tool of the Markov chains theory in various fields of science and technology was growing. There are known the successful attempts to use the approach to investigate physical phenomena (diffusion, heat transfer) [2], technological processes (grinding, mixing, separation) [3], as well as to use it in biology, economy, sociology, etc. The reason for such a widely popular theory of Markov processes is not only a desire to explore natural discrete phenomena and avoidance of the formal description of them using continuous functions and infinitesimals, but also the fact that Markov processes play an important role among the other random processes. They can be often met in practice and have a comparatively simple mathematical description.

The present study is devoted to the description of some results of application of the theory to model some of the problems of chemical kinetics.

2. Justification of the possibility to use the proposed approach

Let us examine the following aspects.

1. Due to the classical theory [1] any chemical reaction can be presented as consequential collisions between separate reacting particles. It allows present the reactions as a discrete processes.
2. For collisions, it is necessary, first, the appearance at the same time at the certain point in space, and secondly, to have proper spatial orientation. Both events have probabilistic character. It should be noted that not every collision leads to reaction: the particles must have enough energy. The factors listed above define the reaction as a stochastic process.
3. At last, an influence of previous event (effective collisions of reacting particles) on further events is typical for chemical reactions. However, it can be supposed that this influence does not go further than through two neighboring events. It means that a chemical reaction is the process, in which the current state depends only on the previous state, in which past and future are mutually independent.

The three mentioned aspects fully characterize the evolution of a chemically reacting system as a discrete Markov chain and allow to recommend the appropriate mathematical tool for the investigation and modelling of chemical reaction kinetics.

3. Brief description of Markov chain

A discrete Markov chain is a mathematical model of a system that has the discrete sample space and changes in discrete moments of time. Usually a Markov chain is presented graphically as an oriented weighted graph (Fig. 1), nodes of which correspond to possible system states A_i , and its arcs correspond to possible transitions of the system from the state i to the state j : $A_i \rightarrow A_j$. Each arc is connected with the transition probability $p_{ij}(k) = p[A_j(k) | A_i(k-1)]$ that is the conditional probability of transition of the system at the k -th time step into the state A_j under the condition that at the previous time step ($k-1$) the system was in the state A_i .

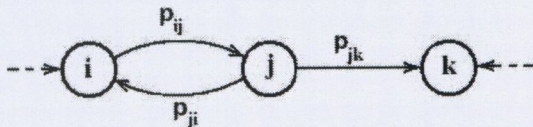


Fig. 1. A piece of a Markov chain graph

Rys. 1. Fragment grafu łańcucha Markowa

The basic operator of the process in a Markov chain is the matrix of transition probabilities:

$$\|P(k)\| = \begin{vmatrix} p_{11}(k) & p_{12}(k) & \dots & p_{1n}(k) \\ p_{21}(k) & p_{22}(k) & \dots & p_{2n}(k) \\ \dots & \dots & \dots & \dots \\ p_{n1}(k) & p_{n2}(k) & \dots & p_{nn}(k) \end{vmatrix} \quad (1)$$

The matrix $\|P(k)\|$ has the important property: the sum of all elements in each row is equal to one:

$$\sum_{j=1}^n p_{ij}(k) = 1 \quad (2)$$

Besides that, at each step the chain is characterized by the row-vector of probabilities of the states in the sample space $|S(k)\rangle$, the elements of which $S_i(k)$ are probabilities of that than at the k -th time step the system is in the state i :

$$|S(k)\rangle = [S_1(k), S_2(k), \dots, S_n(k)] \quad (3)$$

where n is the total number of the system states.

It is obvious that at any moment of time t the sum of all these probabilities is equal to one:

$$\sum_{i=1}^n S_i(k) = 1 \quad (4)$$

The initial state of the system is described by the vector

$$|S(0)\rangle = [S_1(0), S_2(0), \dots, S_n(0)]$$

which is usually given by specific conditions of a process.

Evolution of the system is presented by the set of state vectors for discrete moments of time. Calculation of the state vectors can be done by the following recurrent matrix equality:

$$|S(k+1)\rangle = |S(k)\rangle \cdot \|P(k)\| \quad (5)$$

4. Description of a chemical system in terms of the mathematical tool of the theory of Markov chains

Let us examine the physicochemical sense of mathematical objects that describe a Markov chain.

At the first, let us show that the elements of the matrix of transition probabilities (1) can characterize the intensity of chemical reactions in the system.

Evolution of any system, including a chemical one, occurs due to certain moving forces acting on it. In particular, chemical reactions run under the force of thermodynamic nature. It is natural to assume that the rate and completeness of any reaction depend on the intensity of the forces mentioned. The value that characterizes the intensity of the reaction is its rate. Therefore, the rates can be used as a measure of the intensity of transition of the system from one state to another. It is common to define the rate using the rate constant of a reaction. It is the reaction rate at unit concentration of reacting components. Therefore, the intensity of transitions between the states can be expressed as the reaction rate related to the unit concentration of components. In turn, the intensity of transitions is identical to the probability density of transitions, and the following relationship can be used to define the elements of matrix (1):

$$p_{ij}(k) = v_{ij}(k) \cdot \Delta t \quad (6)$$

where $v_{ij}(k)$ is the rate of reaction that transits the system from the state i into the state j ; Δt is the time step, or transition duration.

In the general case the rate of reaction depends on current concentrations of reacting components. Therefore, the elements of matrix (1) must be calculated at each time step. In other words, when modeling a chemical reaction, we deal with non-homogeneous (non-linear) Markov chains. Only the chemical reactions of the zero and first order are the exception. The elements of the matrix remain constant for them, and the corresponding chain becomes homogeneous.

The sense of the elements of state vector (3) can be defined from the following considerations.

The basic parameter of a chemical process that identically characterizes the state of the system is the concentration of reacting components. The elements of the state vector show the most probable values of the concentrations in a certain moment of time. However, in this case the elements of vector (3) must be not absolute values of the concentrations but their relative values that meet the condition of normalization (4).

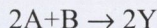
The algorithm of modeling can be presented as follows. First, the time step of modeling Δt must be chosen, and the elements of the initial state vector $|S(0)\rangle$ must be introduced. Next, elements $p_{ij}(0)$ of transition matrix (1) can be calculated using the expressions (6) and (2). Then the next state vector can be calculated using expression (5), i.e., the most probable values of concentrations after the first time step, or the first transition. Then the procedure must be repeated, and so on. The chosen time step does not have to lead to absurd results, i.e., the elements of the transition matrix must be less than one and bigger than zero.

5. Examples of modeling

Let us examine some examples of chemical reactions modeling by means of the theory of Markov chains.

Example 1

Let us examine the simplest case of chemical reaction that goes according to the equation:



where A and B are the initial reactants, Y is the product of the reaction.

Let us consider that, in question, the substances of the system are in stoichiometric quantities.

Suppose that the reacting system has two limit states: state 1 is the initial mixture of A and B, and state 2, in which the system consists of the reaction product Y only. Then state vector (3) for the given reaction will contain only two elements:

$$|S(k)| = [S_1(k), S_2(k)] \quad (7)$$

The graph of the Markov chain for the system is shown in Fig. 2.

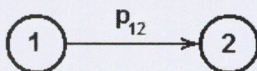


Fig. 2. The graph of the Markov chain for the example 1

Rys. 2. Graf łańcucha Markowa – przykład 1

The following balance equation must be met for the reaction at any moment of time:

$$2 \cdot C_A(k) + 2 \cdot C_B(k) + 3 \cdot C_Y(k) = 2 \cdot C_A(0) + 2 \cdot C_B(0) + 3 \cdot C_Y(0) \quad (8)$$

where $C_A(k)$, $C_B(k)$, $C_Y(k)$ are the current molar concentrations of the substances A, B, Y; $C_A(0)$, $C_B(0)$, $C_Y(0)$ are their initial concentrations.

Expression (8) allows writing equations linking the state vector elements and the concentration in the form:

$$S_1(k) = \frac{2C_A(k) + 2C_B(k)}{2C_A(0) + 2C_B(0) + 3C_Y(0)} \quad S_2(k) = \frac{3C_Y(k)}{2C_A(0) + 2C_B(0) + 3C_Y(0)} \quad (9)$$

Besides, the following can be written:

$$C_A(k) = 2C_B(k) \quad (10)$$

The expressions (9) and (10) allow calculating the concentrations from the state vector values at any time step.

The initial transition probabilities from state 1 to state 2 for the reaction can be calculated as:

$$p_{12}(0) = v_{12}(0) \cdot \Delta t = k_{12} \cdot [C_A(0)]^2 \cdot [C_B(0)] \cdot \Delta t \quad (11)$$

where $v_{12}(0)$ is the initial rate of the reaction; k_{12} is its rate constant.

Due to the reaction conditions probability $p_{21} = 0$. All other elements of the matrix (1) can be calculated using expression (2). At the next time steps the probabilities are calculated by the analogous expressions but using the concentrations at the corresponding time steps.

Fig. 3 shows the results of reaction modelling during 15 time steps of the model time. The initial data were taken as follows: $C_A(0) = 2 \text{ mol/l}$; $C_B(0) = 1 \text{ mol/l}$; $C_Y(0) = 0$; $k_{12} = 4 \cdot 10^3 \text{ l}^2/(\text{mol}^2 \cdot \text{s})$; $\Delta t = 1 \cdot 10^{-5} \text{ s}$.

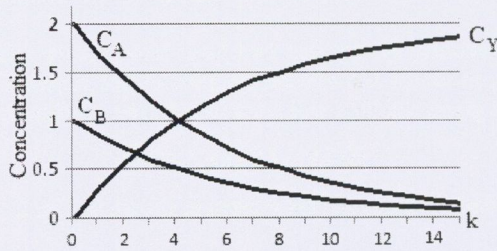


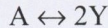
Fig. 3. Kinetics of the reaction (example 1)

Rys. 3. Kinetyka reakcji (przykład 1)

In the example the chemical reaction goes in one direction. The corresponding chain is not ergodic because it has absorbing state from which the reverse transition is forbidden. According to the theory of Markov chains the steady (asymptotic) state of the chain is state 2 that completely agrees with the basic statements of chemical kinetics.

Example 2

Now let us examine a reversible chemical reaction that goes according to the equation:



Let us consider whole limit state 1, when there are only particles of substance A in the system, and limit state 2, when the system consists of particles of substance Y.

The corresponding graph of the chain is shown in Fig. 4.

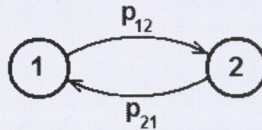


Fig. 4. The graph of the chain for the example 2

Rys. 4. Graf łańcucha – przykład 2

The following balance equation must be met:

$$2C_A(k) + C_Y(k) = 2C_A(0) + C_Y(0) \quad (12)$$

where C_A and C_Y are the molar concentrations of A and Y.

Using (12), the elements of the state vector respectively can be calculated as follows:

$$S_1(k) = \frac{2 \cdot C_A(k)}{2 \cdot C_A(0) + C_Y(0)} \quad S_2(k) = \frac{C_Y(k)}{2 \cdot C_A(0) + C_Y(0)} \quad (13)$$

The transition probabilities that are defined by the rates of corresponding reactions are:

$$p_{12}(i) = k_{12} \cdot \Delta t \quad \text{and} \quad p_{21}(i) = 2 \cdot k_{21} \cdot [C_Y(i)] \cdot \Delta t \quad (14)$$

where k_{12} is the rate constant of the direct reaction, k_{21} is the rate constant for the inverse reaction.

The other elements of matrix (1) can be calculated using relationship (2).

The results of modeling of this reaction kinetics are shown in Fig. 5 for the following initial data: $C_A(0) = 0.5 \text{ mol/l}$; $C_Y(0) = 1 \text{ mol/l}$; $k_{12} = 0.5 \text{ s}^{-1}$; $k_{21} = 2 \text{ l/(mol}\cdot\text{s)}$; $\Delta t = 2.5 \cdot 10^{-2} \text{ [s]}$.

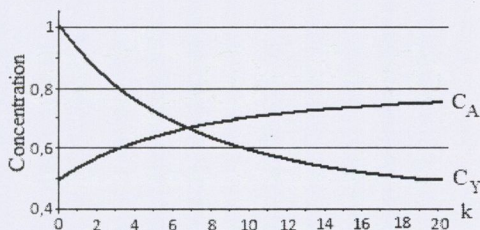


Fig. 5. Kinetics of the reaction (example 2)

Rys. 5. Kinetyka reakcji (przykład 2)

The Markov chain for example 2 is ergodic, i.e., all states of it are reachable. Due to the theory of Markov chains such chain has the steady state (asymptotic) probability distribution, at which all elements of the state vector become constant. Moreover, this distribution does not depend on the initial state. It is shown in Fig. 6 where the kinetic curves are calculated for the same rate constants but at the different initial concentrations.

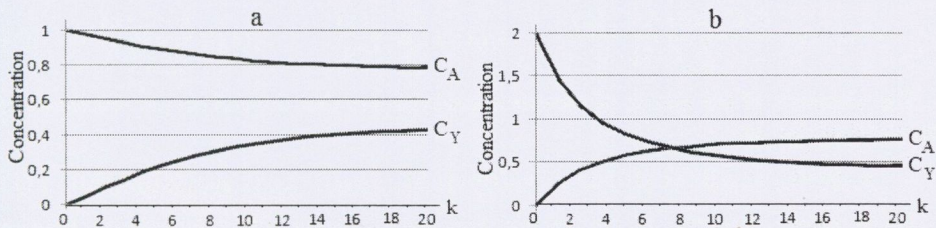


Fig. 6. The reaction kinetics at different initial concentrations

Rys. 6. Kinetyka reakcji przy różnych stężeniach początkowych

On the other hand, from the viewpoint of chemical kinetics, the limit state for a reversible reaction is the equilibrium state. It is also known that if the reactants at a reversible reaction are in the stoichiometric proportion then the equilibrium concentrations do not depend on initial ones. Thus, the results of modelling are in strict

correspondence with the basic foundations of chemical kinetics and do not contradict the classical approach.

Example 3.

The next example concerns the reaction that consists of two stages with the irreversible first stage:



The given system has three limit states. The state 1 corresponds to initial substances A and B, the state 2 corresponds to the intermediate substance M, and the state 3 corresponds to the end products of the reaction X and Y.

The graph of the chain representing the system is shown in Fig. 7.

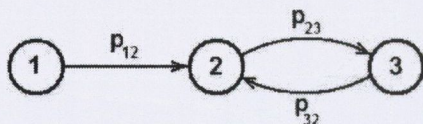


Fig. 7. The graph of the chain for example 3

Rys. 7. Graf łańcucha dla przykładu 3

The following balance equation is valid for the reaction:

$$\begin{aligned} 4 \cdot C_A(k) + 4 \cdot C_B(k) + 6 \cdot C_M(k) + 3 \cdot C_X(k) + 3 \cdot C_Y(k) &= \\ = 4 \cdot C_A(0) + 4 \cdot C_B(0) + 6 \cdot C_M(0) + 3 \cdot C_X(0) + 3 \cdot C_Y(0) &= \sum C(0) \end{aligned} \quad (15)$$

where, as above, C_i are the concentrations of the reactants.

The expressions for the calculation of the state vector elements (now there are 3 elements) have the following form:

$$S_1(k) = \frac{4 \cdot C_A(k) + 4 \cdot C_B(k)}{\sum C(0)} \quad S_2(k) = \frac{6 \cdot C_M(k)}{\sum C(0)} \quad S_3(k) = \frac{6 \cdot C_M(k)}{\sum C(0)} \quad (16)$$

The elements of the matrix of transition probabilities that depend on the reaction rates can be calculated as:

$$p_{12}(i) = k_{12} \cdot [C_A(i)]^2 \cdot [C_B(i)] \cdot \Delta t \quad p_{23}(i) = k_{23} \cdot \Delta t \quad p_{32}(i) = k_{32} \cdot [C_X(i)] \cdot [C_Y(i)] \cdot \Delta t \quad (17)$$

Three more elements of the matrix are zero because direct transitions between corresponding states are impossible:

$$p_{13}(i) = p_{21}(i) = p_{31}(i) = 0 \quad (18)$$

The other elements are calculated using relationship (2).

Results of the modeling are shown in Fig. 8. The following initial data were used in the calculations:

$C_A(0) = 2$ mol/l; $C_B(0) = 1$ mol/l; $C_M(0) = 0$; $C_X(0) = 0$; $C_Y(0) = 0$; $k_{12} = 0.075$ l²/(mol²·s); $k_{23} = 0.05$ s⁻¹; $k_{32} = 1$ l/(mol·s); $\Delta t = 0.5$ s.

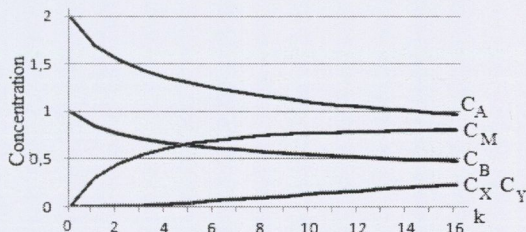


Fig. 8. Kinetics of the reactions for example 3

Rys. 8. Kinetyka reakcji dla przykładu 3

The results shown were calculated for the first 16 time steps only. Analysis of the further process development shows that the concentration of A and B is limited to zero, and the concentrations of M, X and Y tend to constant equilibrium values.

6. Verification of the model

The model verification can be done by comparison of results obtained with different methods.

Let us turn back to the reaction described in example 2. The differential equation of its kinetics has the following form:

$$\frac{dC_A}{dt} = -k_1 \cdot C_A + k_2 \cdot [C_Y(0) + 2 \cdot C_A(0) - 2 \cdot C_A]^2 \quad (19)$$

It allows us to obtain the analytical solution in the form:

$$C_A(t) = \frac{1}{1 - F(t)} \cdot [\lambda_2 - \lambda_1 \cdot F(t)] \quad (20)$$

where:

$$F(t) = \frac{C_A(0) - \lambda_2}{C_A(0) - \lambda_1} \cdot \exp[4 \cdot k_2 \cdot (\lambda_2 - \lambda_1) \cdot t]$$

$$\lambda_1 = \frac{k_1 + 4 \cdot k_2 \cdot [2 \cdot C_A(0) + C_Y(0)]}{8 \cdot k_2} - \frac{1}{8 \cdot k_2} \sqrt{k_1^2 + 8 \cdot k_1 \cdot k_2 \cdot [2 \cdot C_A(0) + C_Y(0)]}$$

$$\lambda_2 = \frac{k_1 + 4 \cdot k_2 \cdot [2 \cdot C_A(0) + C_Y(0)]}{8 \cdot k_2} + \frac{1}{8 \cdot k_2} \sqrt{k_1^2 + 8 \cdot k_1 \cdot k_2 \cdot [2 \cdot C_A(0) + C_Y(0)]}$$

Results of calculation of the reaction kinetics due to analytical solution to equation (20) are presented in Table 1. Concentration of the second component was calculated with balance equation (12). The table also contains the results obtained with the proposed approach. The data obtained with the analytical solution are supposed to be the true ones.

Comparison of the data shows that the proposed model describes the process kinetics with the relative error less than 1.5% that undoubtedly can be estimated as acceptable.

Comparison of computational results of the reaction kinetics obtained by different methods

No	Time	Calculation with (20)		Calculation with the proposed model		Relative error [%]
		$C_A(t)$	$C_Y(t)$	$C_A(t)$	$C_Y(t)$	
		[mol/l]	[mol/l]	[mol/l]	[mol/l]	
	0	0.5	1.0	0.5	1.0	
1	0.025	0.5395	0.9210	0.5438	0.9125	0.78
2	0.05	0.5720	0.8561	0.5786	0.8428	1.16
3	0.075	0.5990	0.8021	0.6069	0.7863	1.32
4	0.1	0.6217	0.7567	0.6302	0.7396	1.37
5	0.125	0.6409	0.7182	0.6497	0.7007	1.37
6	0.15	0.6574	0.6852	0.6661	0.6678	1.32
7	0.175	0.6716	0.6568	0.6801	0.6399	1.26
8	0.2	0.6839	0.6323	0.6920	0.6159	1.20
9	0.225	0.6946	0.6109	0.7024	0.5953	1.12
10	0.25	0.7039	0.5922	0.7113	0.5774	1.05

7. Conclusions

The investigations carried out show that application of the discrete probabilistic model to describe evolution of chemically reacting systems is possible. Despite the fact that majority of researchers follow the traditional methods to model chemical kinetics based on the systems of differential equations the proposed approach is promising. First, the nature of the process is stochasticity. It is known that the rate constant is the product of probabilities of several events (probability of molecules collision, probability of their interaction after collision, etc.). The proposed model allows avoiding the intermediate stage of chemical kinetics description. The physical meaning of the reaction, the driving forces become apparent. Secondly, the numerical solution of differential equations systems of chemical kinetics procedure is much more complex that multiplication of matrices (from computational viewpoint) while analytical solution of the systems is seldom possible.

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