

On One Probabilistic Model of Bimolecular Chemical Reaction

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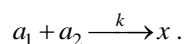
ABSTRACT. In the paper the construction of a probabilistic model of a biochemical reaction with two reagents is reduced to the construction of a probabilistic model of a unimolecular reaction. Explicit forms are obtained for the mathematical expectation and variance of the reagent and product. The numerical example is also considered. © 2018 Bull. Georg. Natl. Acad. Sci.

Key words: chemical reaction, reagent, product, probabilistic model, mathematical expectation, variance

The kinetics of chemical reactions (chemical kinetics) studies the reaction speed. The mathematical theory of chemical kinetics is concerned with the construction of deterministic and probabilistic models which describe chemical processes. These models are used when investigating chemical kinetics. Deterministic models are constructed using differential (integral) equations, while a chemical process is described by means of real continuous functions of time [1-3]. In probabilistic models of chemical kinetics the number of reagent (product) molecules is a random variable. In that case, the problem consists in finding distributions and numerical characteristics of this random variable [4-6].

Nearly all natural processes are of random character. In many spheres of science and applications essential use is made of probabilistic-statistical methods. Using these methods, probabilistic models were constructed and fundamental results were obtained for instance in the investigation of the following issues of chemistry and biology: autocatalytic, unimolecular, bimolecular, monomolecular and chain reactions, population growth, mutation, epidemic theory, gene frequency theory, radio biology and so on [7].

Let us consider the bimolecular chemical reaction of reagents a_1 , a_2 :



Denote the concentrations (numbers of molecules) of these reagents and the product at a moment of time $t \geq 0$ by $a_1(t)$, $a_2(t)$ and $x(t)$, where $a_i(0) > 0$, $i = 1, 2, \dots$, and $x(0) = 0$.

Also denote

$$\begin{aligned}a_1(0) - x(t) &= a_1(t), \\ a_2(0) - x(t) &= a_2(t).\end{aligned}$$

We have

$$\begin{aligned}\sum_{i=1}^2 a_i(0) - 2x(t) &= \sum_{i=1}^2 a_i(t), \\ 2 \min(a_1(0), a_2(0)) + \sum_{i=1}^2 a_i(0) - 2 \min(a_1(0), a_2(0)) - 2x(t) &= \\ &= 2 \min(a_1(t), a_2(t)) + \sum_{i=1}^2 a_i(t) - 2 \min(a_1(t), a_2(t)).\end{aligned}$$

Also denote $\min(a_1(t), a_2(t)) = a(t)$, $t \geq 0$.

Note that the equality

$$\sum_{i=1}^2 a_i(0) - 2a(0) = \sum_{i=1}^2 a_i(t) - 2a(t) \quad (1)$$

is fulfilled for any moment of time $t \geq 0$, where $a(0) = \min(a_1(0), a_2(0))$.

Indeed, we have

$$\sum_{i=1}^2 a_i(t) - 2a(t) = \sum_{i=1}^2 a_i(0) - 2x(t) - 2(a(0) - x(t)) = \sum_{i=1}^2 a_i(0) - 2a(0).$$

The main result is formulated as the following proposition.

Proposition 1. For a bimolecular chemical reaction with participation of the reagents a_1 , a_2 the following relations

$$a(0) - x(t) = a(t), \quad (2)$$

$$V_x(t) = \frac{dx(t)}{dt} = k(a(0) - x(t)) \quad (3)$$

are fulfilled.

Thus, the study of the kinetics of a bimolecular reaction for the reagents a_1 , a_2 is reduced to the study of the kinetics of a unimolecular reaction for the reagent $a = \min(a_1, a_2)$.

Using the equation (8.6) from [7], for the probability

$$P_a(t) = P\{a(t) = a\}, \quad a = 0, 1, \dots, a(0),$$

we obtain the explicit expressions for mathematical expectations and dispersions of the values $a(t)$ and $x(t)$.

Proposition 2. Let a reaction of the form $a \xrightarrow{k} x$ be considered $a(0) - x(t) = a(t)$, $t \geq 0$. Then the following relations

$$E(a(t)) = a(0)e^{-kt} = a(t), \quad (4)$$

$$E(x(t)) = a(0)(1 - e^{-kt}) = x(t), \quad (5)$$

$$D(a(t)) = D(x(t)) = a(0)e^{-kt}(1 - e^{-kt}) \quad (6)$$

are valid.

From (4) and (5) we see that $a(t) \rightarrow a(0)$, $x(t) \rightarrow x(0) = 0$ as $x \rightarrow 0$, while $a(t) \rightarrow 0$, $x(t) \rightarrow x(\infty) = a(0)$ as $t \rightarrow \infty$. Using relations (4) and (5) we can define, at any moment of time $t \geq 0$, the transformation speeds of the reagent $a(t)$ and the product $x(t)$. We have

$$V_a(t) = \frac{da(t)}{dt} = -ka(0)e^{-kt}, \quad (7)$$

$$V_x(t) = \frac{dx(t)}{dt} = ka(0)e^{-kt}, \quad (8)$$

hence for the initial speeds at the moment of time $t = 0$ we obtain respectively $V_a(0) = -ka(0)$ and $V_x(0) = ka(0)$.

For such a parameter of chemical reaction models as the reaction constant k , it can be estimated by the relation

$$k = \frac{1}{t} \ln \frac{a(0)}{a(t)} = \frac{1}{k} \ln \frac{a(0)}{a(0) - x(t)}. \quad (9)$$

Indeed, if there is a possibility to carry out an experiment and obtain empirical data, then for moments t_1, \dots, t_m we will have the sample $(x, k) = (x(t_1), k_1), \dots, (x(t_m), k_m)$. Applying statistical methods, we can obtain by means of this sampling various point (interval) estimates of the reaction speed constant k and also perform regression analysis.

It is of interest to note that by relations (5), (6) and (8) we can calculate the mathematical expectation and dispersion of the reaction speed $V_x(t)$. Indeed, we have

$$V_x(t) = ka(0)e^{-kt} = k[a(0)e^{-kt} - a(0) + a(0)] = -kx(t) + ka(0), \quad (10)$$

$$E(V_x(t)) = -ka(0)(1 - e^{-kt}) + ka(0) = ka(0)e^{-kt} = -E(V_a(t)), \quad (11)$$

$$D(V_x(t)) = k^2 a(0) e^{-kt} (1 - e^{-kt}) = D(V_a(t)). \quad (12)$$

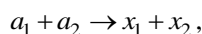
Thus, if we have the estimate of the reaction speed constant k , then for any moment of time $t \geq 0$ we can calculate mathematical expectations (average values) and dispersions (deviation from average values) $E(x(t))$, $D(x(t))$, $E(V_x(t))$ and $D(V_x(t))$ of the values $x(t)$ and $V_x(t)$ which are quite important numerical characteristics for experimenters.

Let us now summarise the main results of this study:

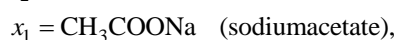
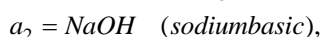
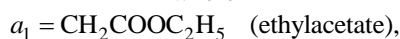
A bimolecular reaction of the form $a_1 + a_2 \xrightarrow{k} x$ for the reagents a_1, a_2 can be described by a unimolecular reaction of the form $a(t) \xrightarrow{k} x(t)$ for one reagent $a = \min(a_1, a_2)$.

For any moment of time $t \geq 0$, we have obtained the explicit analytic expressions of average values and dispersions: $E(x(t))$, $E(V_x(t))$, $D(x(t))$ and $D(V_x(t))$ for the product $x(t)$ and the reaction speed $V_x(t)$.

Example. Let us consider the following chemical reaction



where



Denote the concentrations of the reagents a_1 , a_2 and products x_1 , x_2 at a moment of time $t \geq 0$ by $a_1(t)$, $a_2(t)$, $x_1(t)$, $x_2(t)$. Denote also $\min(a_1(t), a_2(t)) = a(t)$, $t \geq 0$. Note that $x_1(t) = x_2(t)$ ($= x(t)$), $t \geq 0$.

We have the following experimental data:

Table 1.

no.	time	$a_1(0)$	$a_2(0)$	$x(t)$	$a_1(t)$	$a_2(t)$
1	0	8	12	0	8	12
2	10	8	12	3	5	9
3	20	8	12	4	4	8
4	30	8	12	5	3	7
5	40	8	12	5	3	7
6	50	8	12	6	2	6
7	60	8	12	6	2	6
8	100	8	12	7	1	5
9	3000	8	12	8	0	4

According to formula (9) we have:

Table 2.

time	10	20	30	40	50	60	100	3000
k	0.05	0.04	0.03	0.03	0.03	0.02	0.02	0

$$\bar{k} = \frac{1}{8}(0.05 + 0.04 + 0.03 + 0.03 + 0.03 + 0.02 + 0.02 + 0) = 0.03$$

According to formulas (5), (6), (11), (12) we have:

$$Ex(t) = 8(1 - e^{-0.03t}),$$

$$Dx(t) = 8e^{-0.03t}(1 - e^{-0.03t}),$$

$$EV_x(t) = 0.24e^{-0.03t},$$

$$DV_x(t) = 0.0009e^{-0.03t}(1 - e^{-0.03t}).$$

ბიოლოგია

ბიმოლეკულური ქიმიური რეაქციის ერთი ალბათური მოდელის შესახებ

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