

On a Kinetics of a Multimolecular Chemical Reaction

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Abstract— The construction of a probabilistic model of a multimolecular chemical reaction of several reagents is reduced to the construction of a probabilistic model of a unimolecular chemical reaction. New explicit expressions are obtained for product trajectories, reaction speed and also for mathematical expectations and dispersions of these values.

Index Terms— Kinetics of chemical reaction, reagent, product, probabilistic model, reaction speed.

1 INTRODUCTION

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]. 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 [2], [3], [4]. It should be said that in the construction of probabilistic models of chemical and also biological processes an essential role is played by methods of random processes, especially by methods of Markov processes. In particular, models of population growth, epidemics, gene frequency, unimolecular, bimolecular, monomolecular chain reactions and other models [2] were constructed.

In the present paper, for one class of chemical reactions the construction of the probabilistic model of a multimolecular chemical reaction of several reagents is reduced to the construction of the probabilistic model of a unimolecular chemical reaction for the reagent with minimal concentration. Such approach we call the method of the minimum. Explicit expressions are obtained for the product trajectories and the reaction speed, and also for mathematical expectations and dispersions of these values.

Let us briefly consider the deterministic models of unimolecular and bimolecular reactions. Suppose we consider the reaction $a \xrightarrow{k} x$, where $k > 0$ is the reaction speed constant. Denote the concentrations of the reagent a and the product x at a moment of time $t \geq 0$ by $a(t)$ and $x(t)$. It is assumed that $a(0) > 0$, $x(0) = 0$ and $a(0) - x(t) = a(t)$. According to the fundamental axiom of the deterministic theory of chemical kinetics, the reaction speed (product concentration

speed) is proportional to the acting mass, which can be written by means of the equation

$$V_x(t) = \frac{dx(t)}{dt} = k(a(0) - x(t)). \quad (1)$$

From this equation we easily obtain by integration over the time interval $[0, t]$ the following relations

$$x(t) = a(0)(1 - e^{-kt}), \quad (2)$$

$$a(t) = a(0)e^{-kt}. \quad (3)$$

Using these relations, for any moment of time $t \geq 0$ we easily obtain explicit analytic expressions for the speeds of transformation of the reagent a and formation of the product x . Indeed, we obtain

$$V_x(t) = \frac{dx(t)}{dt} = ka(0)e^{-kt}, \quad (4)$$

$$V_a(t) = \frac{da(t)}{dt} = -ka(0)e^{-kt}, \quad (5)$$

whence for the initial speeds we have $V_a(0) = -ka(0)$ and $V_x(0) = +ka(0)$.

Let us now consider the class of bimolecular reactions of the form $a_1 + a_2 \xrightarrow{k} x$ when the collision of a pair of molecules of two reagents results in the formation of one molecule of the product. Denote the concentrations of the reagents and the product at a moment of time $t \geq 0$ by $a_1(t)$, $a_2(t)$ and $x(t)$. It is assumed that $a_1(0) > 0$, $a_2(0) > 0$ and $x(0) = 0$. In that case, an analogue of equation (1) has the form

$$V_x(t) = \frac{dx(t)}{dt} = k[(a_1(0) - x(t))(a_2(0) - x(t))], \quad (6)$$

whence by integration over the time interval $[0, t]$ it readily follows that

$$x(t) = a_1(0)a_2(0) \frac{e^{kt(a_2(0)-a_1(0))} - 1}{a_2(0)e^{kt(a_2(0)-a_1(0))} - a_1(0)}. \quad (7)$$

From this we can easily obtain the reaction speed expression for any moment of time $t \geq 0$.

It should be said that if the concentrations of the reagents a_1 and a_2 are equal, $a_1(0) = a_2(0)$, then from (7) we obtain an uncertainty of the form $0/0$. Moreover, in the case of three reagents, the problem of obtaining an explicit expression for the product $x(t)$ from the analogue of equation (6) is a rather difficult mathematical problem which, in principle, cannot be

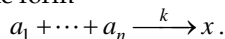
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solved analytically.

2 RESULTS AND THE DISCUSSION

We will now try to construct the probabilistic model of a multimolecular chemical reaction by using a different approach to finding an explicit expression of the product trajectory.

Let us consider the multimolecular chemical reaction of reagents a_1, \dots, a_n of the form



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

Also denote

$$\begin{aligned} a_1(0) - x(t) &= a_1(t) \\ &\dots\dots\dots \\ a_n(0) - x(t) &= a_n(t). \end{aligned} \quad (8)$$

From (8) we have

$$\sum_{i=1}^n a_i(0) - nx(t) = \sum_{i=1}^n a_i(t). \quad (9)$$

Let us rewrite relation (9) in the following form, the validity of which is easy to verify:

$$\begin{aligned} &n \cdot \min(a_1(0), \dots, a_n(0)) \\ &+ \sum_{i=1}^n a_i(0) - n \cdot \min(a_1(0), \dots, a_n(0)) - nx(t) \\ &= n \cdot \min(a_1(t), \dots, a_n(t)) \\ &+ \sum_{i=1}^n a_i(t) - n \cdot \min(a_1(t), \dots, a_n(t)), \end{aligned} \quad (10)$$

where for $t \geq 0$, $\min(a_1(0), \dots, a_n(0))$ is a minimal value among the values $a_i(t)$, $i = 1, \dots, n$. Also denote $\min(a_1(t), \dots, a_n(t)) = a(t)$, $t \geq 0$.

Note that in relation (10) the equality

$$\sum_{i=1}^n a_i(0) - n \cdot a(0) = \sum_{i=1}^n a_i(t) - n \cdot a(t) \quad (11)$$

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

Indeed, we have

$$\begin{aligned} &\sum_{i=1}^n a_i(t) - n \cdot a(t) \\ &= \sum_{i=1}^n a_i(0) - n \cdot x(t) - n \cdot (a(0) - x(t)) \\ &= \sum_{i=1}^n a_i(0) - n \cdot a(0). \end{aligned}$$

Let us once more formulate our conjectures and the main result.

Conjecture 1. One molecule of the product x is formed only after the collision of one molecule of the reagents a_1, \dots, a_n .

Conjecture 2. Instead of the product of concentrations (acting masses) of the reagents a_1, \dots, a_n , as the acting mass we take the sum of the number of molecules of the reagents $a_1(t) + \dots + a_n(t)$, $t \geq 0$.

Conjecture 3. We use the fundamental axiom of the deterministic theory of chemical kinetics, according to which the speed of product formation is proportional to the acting mass. This is the so-called law of acting masses.

The main result is formulated as the following proposition.

Proposition 1. Let Conjectures 1-3 be fulfilled. Then for a multimolecular chemical reaction with participation of the reagents a_1, \dots, a_n the following relations are fulfilled:

$$a(0) - x(t) = a(t), \quad (12)$$

$$V_x(t) = \frac{dx(t)}{dt} = k[a(0) - x(t)]. \quad (13)$$

where $a(0) = \min(a_1(0), \dots, a_n(0))$.

Thus the study of the kinetics of a multimolecular reaction for the reagents a_1, \dots, a_n is reduced to the study of the kinetics of a unimolecular reaction for the reagent $a = \min(a_1, \dots, a_n)$. As to relation (12) it is directly obtained by relations (10) and (11).

For (11) and (12) as an illustration consider a numerical example. Let number of reagents is $n = 2$, $a_1(0) = 8$, $a_2(0) = 12$. Then we have the following table.

TABLE 1

t	$a_1(0)$	$a_2(0)$	$x(t)$	$a_1(t)$	$a_2(t)$	$a_1(0) + a_2(0) - 2a(0)$	$a_1(t) + a_2(t) - 2a(t)$
0	8	12	0	8	12	$8 + 12 - 2 \cdot 8 = 4$	$8 + 12 - 2 \cdot 8 = 4$
1	8	12	3	5	9	4	$5 + 9 - 2 \cdot 5 = 4$
2	8	12	5	3	7	4	$3 + 7 - 2 \cdot 3 = 4$
\vdots	\vdots	\vdots	\vdots	\vdots	\vdots	\vdots	\vdots
∞	8	12	8	0	4	4	$0 + 4 - 2 \cdot 0 = 4$

Conjecture 4. The reagents a_1, \dots, a_n are statistically independent and the probability of the reverse reaction $x \xrightarrow{k} a = \min(a_1, \dots, a_n)$ is equal to zero.

Using equation (8.6) from [2], 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 $a(0) - x(t) = a(t)$, $t \geq 0$, and Conjectures 1-4 be fulfilled. Then the following relations are valid:

$$E(a(t)) = a(0)e^{-kt} = a(t), \quad (14)$$

$$E(x(t)) = a(0)(1 - e^{-kt}) = x(t), \quad (15)$$

$$D(a(t)) = D(x(t)) = a(0)e^{-kt}(1 - e^{-kt}). \quad (16)$$

From (14) and (15) we see that $a(t) \rightarrow a(0)$, $x(t) \rightarrow x(0) = 0$ as $t \rightarrow 0$, while $a(t) \rightarrow 0$, $x(t) \rightarrow x(\infty) = a(0)$ as $t \rightarrow \infty$. Using relations (14) and (15) we can define, at any moment of time $t \geq 0$, the transfor-

mation speeds of the reagent $a(t)$ and the product $x(t)$. We have

$$V_a(t) = \frac{da(t)}{dt} = -ka(0)e^{-kt}, \quad (17)$$

$$V_x(t) = \frac{dx(t)}{dt} = +ka(0)e^{-kt}, \quad (18)$$

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

Note that we were able to obtain expressions (14) and (15) by using the analogue of equation (1) for the values $k \min(a_1(t), \dots, a_n(t))$ and $x(t)$. It should also be said that the constructed probabilistic models (14) and (15) enable us to calculate dispersions (16) which are very important characteristics for the analysis of chemical kinetics.

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

$$k = \frac{1}{t} \ln \frac{a(0)}{a(0) - x(t)}. \quad (19)$$

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 (integral) estimates of the reaction speed constant k and also perform regression analysis.

It is of interest to note that by relations (15), (16) and (18) we can calculate the mathematical expectation and dispersion of the reaction speed $V_x(t)$. Indeed, we have

$$\begin{aligned} V_x(t) &= ka(0)e^{-kt} = k[a(0)e^{-kt} - a(0) + a(0)] \\ &= -kx(t) + ka(0), \\ E(V_x(t)) &= -ka(0)(1 - e^{-kt}) + ka(0) \\ &= ka(0)e^{-kt} = -E(V_a(t)), \end{aligned}$$

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

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 (deviations 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:

1. A multimolecular reaction of the form $a_1 + \dots + a_n \xrightarrow{k} x(t)$ for the reagents a_1, \dots, a_n can be described by a unimolecular reaction of the form $a(t) \xrightarrow{k} x(t)$ for one reagent $a = \min(a_1, \dots, a_n)$ with the help of model (15).
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 $V_x(t)$.

Corollary 1. If the initial numbers of molecules (initial concentrations) of the reagents a_1, \dots, a_n coincide $a_1(0) = \dots = a_n(0)$, then, in this case too, the unimolecular reaction model has form (15).

Corollary 2. It is easy to see that model (15) of a multimolecular chemical reaction can be successfully used also in the case when product molecules are formed as a result of collision of different numbers of molecules of the reagents participating in the chemical reaction.

At last consider the graphs of values $E(x(t))$, $E(a(t))$, $E(V_x(t))$ and $E(V_a(t))$. We have

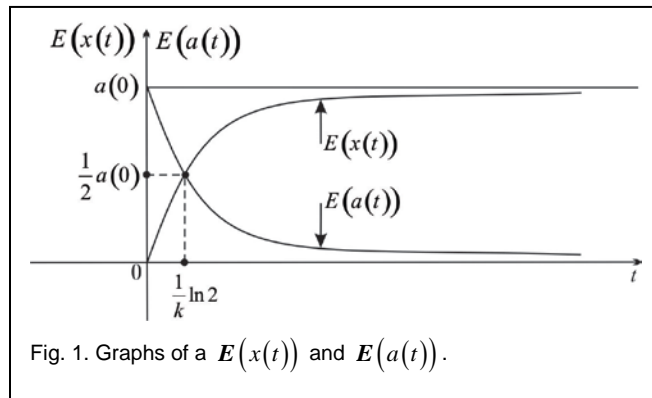


Fig. 1. Graphs of a $E(x(t))$ and $E(a(t))$.

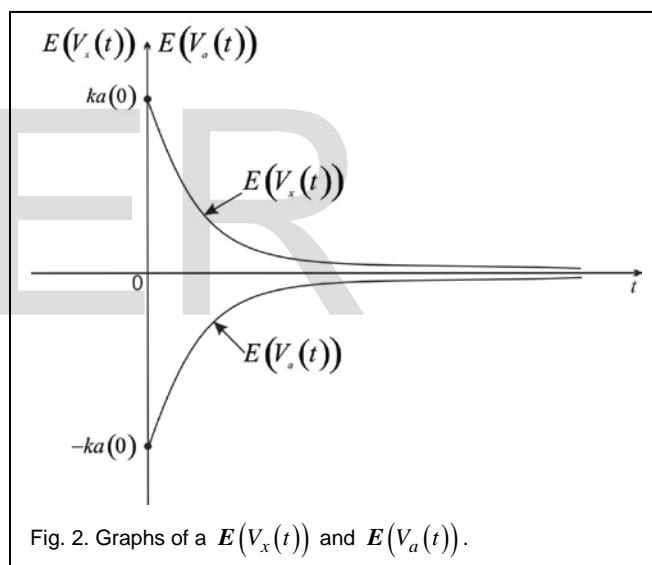
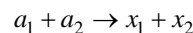


Fig. 2. Graphs of a $E(V_x(t))$ and $E(V_a(t))$.

Example. Let us consider the following chemical reaction



where

$a_1 = \text{CH}_3\text{COOC}_2\text{H}_5$ (ethylacetate),

$a_2 = \text{NaOH}$ (sodium basic),

$x_1 = \text{CH}_3\text{COONa}$ (sodiumacetate),

$x_2 = \text{C}_2\text{H}_5\text{OH}$ (alcohol).

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 dates

TABLE 2

N	$t \text{ min}$	$a_1(0)$	$a_2(0)$	$x(t)$	$a_1(t)$	$a_2(t)$
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 3

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

$$\begin{aligned} Ex(t) &= 8(1 - e^{-0.03t}), \\ Dx(t) &= 8e^{0.03t}(1 - e^{-0.03t}), \\ EV_x(t) &= 0.24e^{-0.03t}, \\ DV_x(t) &= 0.0009e^{-0.03t}(1 - e^{-0.03t}). \end{aligned}$$

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