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Biochemistry

On One Stochastic Model of a Chemical Reaction

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ABSTRACT. Nearly all natural reactions 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 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, radiobiology, and so on. In this paper a chemical reaction of first order is considered when the reagent concentration is distributed by the binomial law. New expressions are obtained for the mathematical expectation and variance of the reagent concentration and product. A stochastic model of a first order reaction is constructed.
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Key words: *chemical reaction, concentration, velocity, mean, variance, binomial distribution, stochastic model.*

The motion and velocity of each particle or a system of particles obey certain laws. For instance in classical mechanics the behavioral laws of particles in time and space are deterministic – the current state of a particle uniquely determines its future states. On the other hand, for instance, Brownian motion laws, variation of energy levels of elementary particles, motion laws in quantum mechanics and others are stochastic – the current state of a particle can determine only the probability of future states of a particle. Besides, deterministic models are described by real functions of time, whereas stochastic models are described by random (stochastic) processes [1-3]. Note that the mathematical theory of Brownian motion as a stochastic process was constructed by N. Wiener. This theory underlies the modern stochastic integral and differential calculus (stochastic analysis) [6-8].

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 [1, 4, 5].

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Let us consider the unimolecular reaction $A \xrightarrow{k} B$, where under certain conditions the substance A (reagent) transforms irreversibly to the substance B (product). A reaction velocity constant $k > 0$ depends on the conditions and kind of reaction. Let the concentration of the reagent A be described by the function $A(t)$, and that of the product B by the function $B(t)$, $t \geq 0$. Assume that in this chemical reaction of first order $A(0) = A_0 > 0$, $B(0) = 0$ and the equality

$$A_0 - A(t) = B(t), \quad t \geq 0 \tag{1}$$

is fulfilled for any moment of time.

According to the deterministic model of a first order chemical reaction, the reagent and product concentrations are described respectively by the following functions of time [3]

$$A(t) = A_0 e^{-kt}, \ t \geq 0 \tag{2}$$

$$B(t) = A_0 \left(1 - e^{-kt}\right), \ t \geq 0 \tag{3}$$

Note that $A(t)$ is a decreasing function of time since the first derivative with respect to time is $A_t'(t) = -kA_0 e^{-kt} < 0$. Clearly, this fact is natural. Also, $A(t)$ is convex from below – $A_{tt}''(t) = k^2 A_0 e^{-kt} > 0$. We obtain analogously that $B(t)$ is an increasing, convex from the above function since we have $B_t'(t) = kA_0 e^{-kt} > 0$, $B_{tt}''(t) = -k^2 A_0 e^{-kt} < 0$. Let us consider some moment of time $t = t_0$ and draw tangent lines for the functions $A(t)$ and $B(t)$ at the points $M\left(t_0, A(t_0)\right)$ and $N\left(t_0, B(t_0)\right)$, respectively. Equations of these tangent lines have the form

$$f(t) = A_t'(t_0)t + A(t_0) - A_t'(t_0) \cdot t_0,$$
$$g(t) = B_t'(t_0)t + B(t_0) - B_t'(t_0) \cdot t_0.$$

For the points $\left(0, A(0)\right)$ and $\left(0, B(0)\right)$ the tangent lines have the following form:

$$f_0(t) = A_t'(0)t + A_0, \tag{4}$$

$$g_0(t) = B_t'(0)t. \tag{5}$$

The angular coefficients $A_t'(t_0)$ and $B_t'(t_0)$ of these linear equations express the concentration velocities of $A(t)$ and $B(t)$, respectively, at any moment of time $t_0 \geq 0$. It is obvious that at any moment of time $t \geq 0$ we have $A_t'(t) + B_t'(t) = 0$, i.e. the sum of instantaneous concentrations $A(t)$ and $B(t)$ at any moment of time $t \geq 0$ is equal to zero. From (2)-(5) we immediately obtain for the initial velocities of reagent A and product B that $A_t'(0) = -kA_0$, $B_t'(0) = kA_0$. Note also that the graphs of the functions $A(t)$ and $B(t)$ intersect at the point $t = \frac{1}{k}\ln 2$ at which we have $A\left(\frac{1}{k}\ln 2\right) = B\left(\frac{1}{k}\ln 2\right) = \frac{1}{2}A_0$. In other words, the moment of time $t = \frac{1}{k}\ln 2$ is the moment of the half reaction of the reagent A (half reaction of the product B). Moreover, the line $A(t) = 0$ is the asymptote of the function $A(t)$, whereas the line $B(t) = A_0$ is the asymptote of the function $B(t)$. The functions $A(t)$ and $B(t)$ are mutually symmetric with respect to the line $A(t) = B(t) = \frac{1}{2}A_0$. Analogously, the line $A_t'(t) = B_t'(t) = 0$ is the asymptote for the velocity functions $A_t'(t)$ and $B_t'(t)$ and these functions are mutually symmetric with respect to this line. The reaction velocity $A_t'(t)$ of the reagent A always increases and the reaction velocity $B_t'(t)$ of the product B always decreases.

To construct the stochastic model of a unimolecular reaction we assume that the concentration of the reagent A as a random process A_t is defined by the formula

$$A_t = A_0 + \int_0^t r(s)\,ds + \int_0^t \sigma(s)\,dw_s \qquad (6)$$

where the first integral is the usual Riemann integral and the second (stochastic) integral is taken over the Wiener process [8]. The functions of time $r(t)$ and $\sigma(t)$ are unknown and have to be found. At every fixed moment of time $t \geq 0$ the value A_t is a random variable whose possible values are $x = 0,1,\ldots,A_0$. We should find the distribution of this random variable.

In many problems of biology and chemistry there exist definite connections between deterministic and stochastic models. For instance in population growth models the mean value of a population size coincides with the population size function for a deterministic process of population growth [1]. Due to this fact we assume that the random variable A_t has the binomial distribution

$$P(A_t = x) = C_{A_0}^x p^x (1-p)^{A_0 - x} \qquad (7)$$

where the probability of "success" is $p = e^{-kt}$. Note that the distribution measure $\mu_t(x) = P(A_t = x)$ is smooth, has the logarithmic derivative with respect to the parameter t

$$\mu_t'(x) = C_{A_0}^x \left(1-e^{-kt}\right)^{A_0-x-1}\left(xe^{-kt} - x + A_0 e^{-kxt} - xe^{-kxt}\right).$$

This discrete measure with alternating signs is absolutely continuous with respect to the measure $\mu_t(x)$ and the Radon-Nycodim derivative is written as

$$\ell_t(x) = \frac{d\mu_t'(x)}{d\mu_t(x)} = \frac{ke^{kt(x+1)}}{e^{kt}-1}\left(xe^{-kt} - x + A_0 e^{-kxt} - xe^{-kxt}\right).$$

Hence it follows that all measures $\mu_t(x)$ are equivalent. This practically means that the process A_t cannot be "very bad", i.e. we should not expect any large deviations from the averaged process $E(A_t)$. By virtue of (2) and (7), for the mathematical expectation and variance of A_t we can write

$$E(A_t) = A(t) = A_0 e^{-kt} \qquad (8)$$

$$D(A_t) = A_0 e^{-kt}\left(1-e^{-kt}\right) = A(t)\left(1-e^{-kt}\right) \qquad (9)$$

It is easy to see that B_t has the following binomial distribution with probability of "success" $1-e^{-kt}$

$$P(B_t = x) = C_{A_0}^x \left(1-e^{-kt}\right)^x \left(e^{-kt}\right)^{A_0 - x} \qquad (10)$$

and we obtain

$$E(B_t) = A_0\left(1-e^{-kt}\right) = B(t) \qquad (11)$$

$$D(B_t) = A_0\left(1-e^{-kt}\right)e^{-kt} = D(A_t) \qquad (12)$$

Thus, in the deterministic model (2), (3) the functions $A(t)$ and $B(t)$ are the averaged trajectories of the processes A_t and B_t. The dispersions of these processes coincide, have a maximum at the moment of time $t = \dfrac{\ln 2}{2}$ and a unique point of inflection at the moment of time $t = \dfrac{\ln 4}{k}$.

Note that according to (8) and (11) the velocities of the concentrations $A(t)$ and $B(t)$ coincide with the velocities of the average concentration values of the processes A_t and B_t, respectively: $A_t'(t) = \left(E(A_t)\right)_t'$, $B_t'(t) = \left(E(B_t)\right)_t'$. Moreover, A_t and B_t are the so-called Markov processes, discrete in space and continuous in time. A_t is the process of pure death and B_t is the process of birth. Note that expressions (8), (9) are obtained by a different technique when A_t has a distribution different from (7) [1].

Let us now find the functions $r(t)$ and $\sigma(t)$. From (6) we have

$$E(A_t) = A_0 + \int_0^t r(s)\,ds = A_0 e^{-kt} \qquad (13)$$

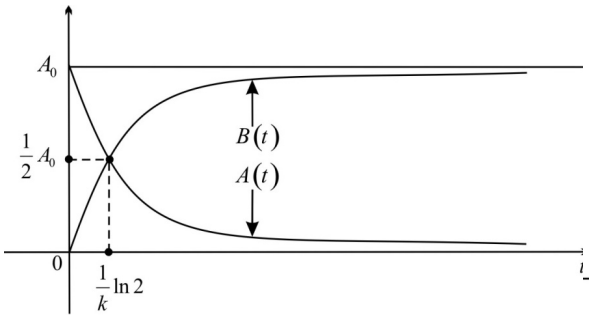

Fig. 1. Concentration of functions of a reagent and a product.

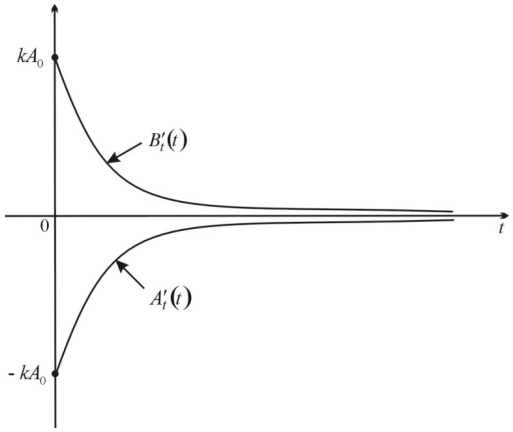

Fig. 2. Concentration of velocities of a reagent and a product.

$$D(A_t) = \int_0^t \sigma^2(s)\,ds = A_0 e^{-kt}\left(1 - e^{-kt}\right). \quad (14)$$

From (15), (14) we easily find

$$r(t) = -kA_0 e^{-kt} = -kA_t,$$
$$\sigma^2(t) = kA_t\left(2e^{-kt} - 1\right).$$

Thus for the process A_t we obtain the stochastic integral representation

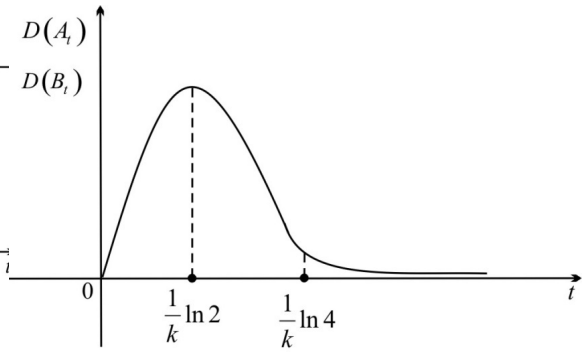

Fig. 3. Variance of concentration of a reagent and a product.

$$A_t = A_0 - k\int_0^t A_s\,ds + k^{\frac{1}{2}}\int_0^t \sqrt{A_s\left(2e^{-ks} - 1\right)}\,dw_s \quad (15)$$

An analogous representation can be easily obtained for the process B_t, too. Note that if there is a possibility to observe the course of the process A_t and to obtain the sampling $A_{t_1}, \ldots, A_{t_n}$, then one can solve various statistical problems as the behavior of the process A_t. Also note that the found functions $r(t)$ and $\sigma(t)$ satisfy the conditions which ensure the existence of representation (6).

For functions $A(t)$, $B(t)$, $A_t'(t)$, $B_t'(t)$, $D(A_t)$ and $D(B_t)$ we have the graphs (Figs. 1-3).

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ბიოქიმია

ქიმიური რეაქციის ერთი სტოქასტური მოდელის შესახებ

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თითქმის ყველა ბუნებრივ რეაქციას აქვს შემთხვევითი ხასიათი. მეცნიერებისა და პრაქტიკის ბევრ სფეროში არსებითად გამოიყენება ალბათურ-სტატისტიკური მეთოდები. ამ მეთოდებით აგებულია ალბათური მოდელები და მიღებულია ფუნდამენტური შედეგები ქიმიისა და ბიოლოგიის შემდეგ პრობლემებში: ავტოკატალიზურ, უნიმოლეკულურ, ბიმოლეკულურ, მონომოლეკულურ და ჯაჭვურ რეაქციებში, პოპულაციის ზრდაში, მუტაციაში, ეპიდემიის თეორიაში, გენების სიხშირეთა თეორიაში, რადიობიოლოგიაში და სხვა. ამ ნაშრომში განხილულია პირველი რიგის ქიმიური რეაქცია, როდესაც რეაგენტის კონცენტრაცია განაწილებულია ბინომური კანონით. მიღებულია რეაგენტისა და პროდუქტის კონცენტრაციების მათემატიკური ლოდინისა და დისპერსიის ცხადი გამოსახულებები. აგებულია აგრეთვე პირველი რიგის რეაქციის სტოქასტური მოდელი.

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