On the Autoregression Model of a Multimolecular Chemical Reaction

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Abstract— Unimolecular chemical reaction model is considered. For the reaction product process autoregression scheme is proposed and representations of the reaction speed are obtained.

Index Terms— Chemical reaction, reaction speed, lifetime, autoregressive model, product, reagent, probabilistic model.

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], [5]. 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, epidemies, gene frequency, unimolecular, bimolecular, monomolecular chain reactions and other models [2] were constructed.

In [4] 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 and explicit expressions are obtained for product trajectories, reaction speed and also for mathematical expectations and dispersions of these values.

In present paper we consider a probabilistic model of unimolecular chemical reaction and for the reaction product process propose first order autoregressive model. Then regression parameters are estimated and chemical reaction lifetime is calculated.

2 Results and the Discussion

In present paper we consider a probabilistic model of unimolecular chemical reaction and for the reaction product process propose first order autoregressive model. Then regression parameters are estimated and chemical reaction lifetime is calculated.

Let us consider the following single-molecule chemical reaction for reagent a

$$a \xrightarrow{k} x, \tag{1}$$

where $k>0$ is the reaction speed constant. Denote the concentrations (number of molecules) of the reagent a and the product x at the moment of time t, $0\le t<\infty$, by $a(t)$ and $x(t)$, where $a(0)>0$, $x(0)=0$. We assume that product $x(t)$ satisfies the following equation [1], [2],

$$x(T-1)=a(0)\left(1-e^{-k(T-1)}\right), \tag{2}$$

here T is the lifetime of reaction.

Using equation (8.6) from [2] for the probability

$$a(t)P_a(t)=P\left(a(t)=a\right),\quad a=0,1,\ldots,a(0)$$

we consider the following model of reagent a and for product x:

$$Ea(t)=a(t)=\frac{T-t}{T}a(0)e^{-kt}, \tag{3}$$

$$Ex(t)=x(t)=a(0)\left(1-\frac{T-t}{T}a(0)e^{-kt}\right), \tag{4}$$

where $0\le t\le T$.

Note, that from Equations (1)-(2), we have

$$a(0)=a(t)+x(t),$$

$$a(t)\to a(0),\quad \text{when } t\to 0,$$

$$a(t)\to 0,\quad \text{when } t\to T,$$

$$x(t)\to 0,\quad \text{when } t\to 0,$$

$$x(t)\to a(0),\quad \text{when } t\to T.$$

$$V_a(t)=\frac{da(t)}{dt}=-\left(\frac{1}{T}+\frac{T-t}{T}k\right)a(0)e^{-kt}, \tag{5}$$

$$V_x(t)=\frac{dx(t)}{dt}=\left(\frac{1}{T}+\frac{T-t}{T}k\right)a(0)e^{-kt}. \tag{6}$$

Whence, for the initial speeds, we obtain, respectively:

$$V_a(0)=-\left(\frac{1}{T}+k\right)a(0), \tag{7}$$

$$V_x(0)=\left(\frac{1}{T}+k\right)a(0). \tag{8}$$

Note, that from (3)-(8), at $T\to\infty$ we have

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$$a(t)\to a(0)e^{-kt},\quad x(t)\to a(0)\left(1-e^{-kt}\right),$$
$$V_a(t)\to -ka(0)e^{-kt},\quad V_x(t)\to ka(0)e^{-kt},$$
$$V_0(t)\to -ka(0),\quad V_x(t)\to ka(0).$$

Consider the graphs of functions $a(t)$, $x(t)$, $V_a(t)$ and $V_x(t)$. We have

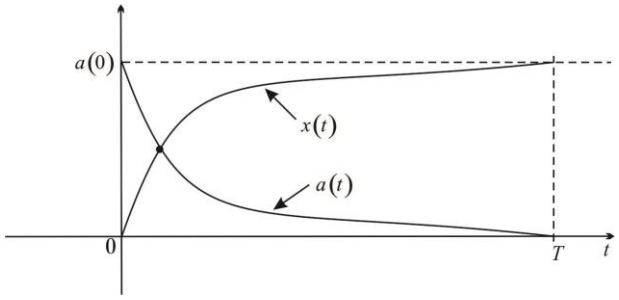

Fig. 1

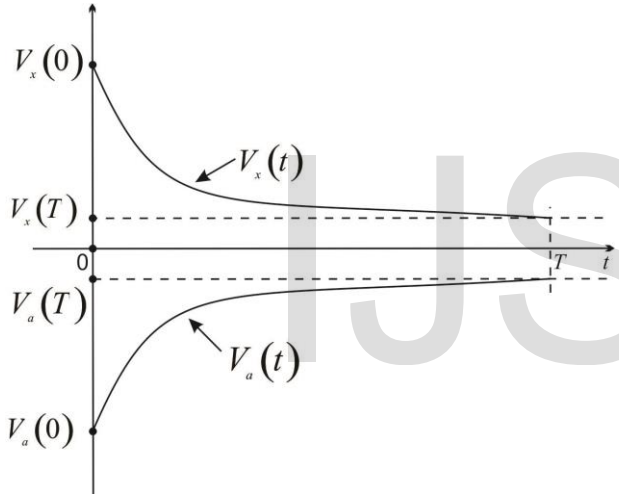

Fig. 2.

In the chemical and biological tests one of the most important question for experimenter is the estimation of reaction life time, i.e. evaluation of the moment when reaction is over. To resolve this task the various type of linear and nonlinear autoregressive models can be applied, as well as exponential model and others. Since we have explicit analytical model describing unimolecular chemical reaction quite adequately [2], [3], [4], [5], then for the constructing autoregressive models we use well developed method in the time series theory [6].

We apply first order autoregressive model that means the following: let's say we do some chemical testing and make n measurement at equally distant moments of time, $(t_1,t_2,\ldots,t_n)$ Therefore we have sample of size n, so that pairs of numbers

$$\left(t,x(t)\right)=\left(t_1,x(t_1)\right),\ldots,\left(t_n,x(t_n)\right). \tag{9}$$

Note, that pair sequence (9) can be rewrited in form

$$\left(t,x(t)\right)=\left(1,x(1)\right),\ldots,\left(n,x(n)\right).$$

The first order autoregressive model is

$$x(t+1)=\alpha+\beta x(t) \tag{10}$$

where α and β are unknown coefficients. Consider the expression

$$g(\alpha,\beta)=\sum_{i=1}^{n-1}\left(x(i+1)-\alpha-\beta x(i)\right)^2. \tag{11}$$

Consider also two partial derivatives of (11) by parameters α and β and let them be zero

$$\frac{\partial g(\alpha,\beta)}{\partial\alpha}=\sum_{i=1}^{n-1}\frac{\partial}{\partial\alpha}\left(x(i+1)-\alpha-\beta x(i)\right)^2=0\ , \tag{12}$$

$$\frac{\partial g(\alpha,\beta)}{\partial\beta}=\sum_{i=1}^{n-1}\frac{\partial}{\partial\beta}\left(x(i+1)-\alpha-\beta x(i)\right)^2=0\ , \tag{13}$$

and solve the system (12), (13), for parameters.

Theorem. Let the unimolecular chemical reaction is described by (1), (2), (10). Then for the lifetime T of reaction the following formula is true

$$T=1+\frac{1}{k}\ln\frac{\beta a(0)}{\alpha+(1-\beta)a(0)}.$$

Proof. According to (10) and taking into account $x(t)=a(0)$, we have

$$x(T)=a(0)=\alpha+\beta x(T-1) \tag{14}$$

Inserting (2) in (14) we get

$$a(0)=\alpha+\beta a(0)-\beta a(0)e^{-k(T-1)}$$

Hence

$$\beta a(0)e^{-k(T-1)}=\alpha+\beta a(0)-a(0),$$
$$e^{k(T-1)}=\frac{\beta a(0)}{\alpha+\beta a(0)-a(0)}.$$

Taking logarithm on both sides we have

$$kT-k=\ln\frac{\beta a(0)}{\alpha+(1-\beta)a(0)},$$

and finally we obtain the formula for reaction time T

$$T=1+\frac{1}{k}\ln\frac{\beta a(0)}{\alpha+(1-\beta)a(0)}.$$

Remark. It is possible to get analogical estimation for T using model of $a(t)$.

Namely

$$a(t)=\gamma+\delta a(t-1).$$

Then analogically of formulas (10), (11) we determine unknown coefficients γ and δ. In this case $a(T)=0$ [5] and we get

$$a(T)=0=\gamma+\delta a(0)e^{-k(T-1)},$$
$$\gamma e^{k(T-1)}=-\delta a(0),$$
$$kT-k=\ln\left(-\frac{\delta a(0)}{\gamma}\right)$$

and, finally,

$$T = 1 + \frac{1}{k} \ln\left(-\frac{\delta a(0)}{\gamma} \right).$$

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