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Stochastic Model for Autocatalytic Reaction

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In the autocatalytic reaction A→B, the rate of production of B is not only proportional to the concentration of reactant A, but also to the concentration of product B; in other words the reaction catalyzes itself. Hence, this reaction may be regarded as a second-order reaction.

To construct a stochastic model for the autocatalytic reaction, let the random variable $X(t)$ represent the number of molecules of the product B at time t, and let us denote the probability of finding x molecules of B in the reaction system at time t by $P(x\,;t)=\text{Prob}\{X(t)=x\}$, $x=b,\ b+1,\cdots,\ b+a$, where $X(0)=b(\geq 1)$ and $a(\geq b)$ is the total number of molecules of reactant A. If, then, the transition probability that one B-molecule will be produced in the interval $(t, t+\Delta t)$ is given by $k\{a-(x-b)\}x\Delta t+o(\Delta t)$, it follows from the stochastic theory of second-order reaction kinetics[1-3] that the probability $P(x\,;t)$ satisfies the set of differential-difference equations

$$\frac{\mathrm{d}}{\mathrm{d}t}P(x;t)=k\{a-[(x-1)-b]\}(x-1)P(x-1;t)-k\{a-(x-b)\}xP(x;t) \qquad (1)$$

$$(b\leq x\leq b+a)$$

where k is the rate constant and $P(b-1\,;t)=0$ has been assumed for all $t\geq 0$. This is to be solved with the initial conditions

$$\begin{aligned}P(x;0)&=1 \quad \text{for } x=b\\ &=0 \quad \text{otherwise.}\end{aligned}$$

We then have the probability distribution, for $b\geq x\geq(a+b)/2$ $(a+b$, even) or $b\geq x\geq(a+b-1)/2$ $(a+b$, odd),

$$\begin{aligned}P(x;t)&=\frac{a!(x-1)!}{(a+b-x)!(b-1)!}\sum_{i=b}^{x}(-1)^{i-b}(a+b-2i)\\ &\quad\times\frac{(a+b-x-i-1)}{(a-i)!(i-b)!(x-i)!}\exp\{-k(a+b-i)it\}\\ &=\frac{a!(x-1)!}{(a+b-x)!(b-1)!}\sum_{j=0}^{x-b}(-1)^{j}(a-b-2j)\\ &\quad\times\frac{(a-x-j-1)!}{(a-b-j)!j!(x-b-j)!}\\ &\quad\times\exp\{-k(a-j)(b+j)t\} \qquad (2)\end{aligned}$$

which has been derived by the method of Laplace transform.

The restriction $b\geq x\geq(a+b)/2$ or $b\geq x\geq(a+b-1)/2$ has been assumed for the study of the initial stage of reaction. In this stage, it follows that the approximations

$$\begin{aligned}\frac{a!}{(a+b-x)!}&=a^{x-b}\prod_{i=1}^{x-b-1}\left(1-\frac{i}{a}\right)\\ &\simeq a^{x-b}\end{aligned}$$

and

$$\begin{aligned}&(a-b-2j)\frac{(a-x-j-1)!}{(a-b-j)!}\\ &=a\left(1-\frac{b+2j}{a}\right)\Big/a^{x-b+1}\prod_{i=0}^{x-b}\left(1-\frac{b+j+i}{a}\right)\\ &\simeq a^{-(x-b)}\end{aligned}$$

hold for sufficiently large $a(\gg b)$. Moreover, we assume that

$$\begin{aligned}k(a-j)(b+j)&=ka\left(1-\frac{j}{a}\right)(b+j)\\ &\simeq\lambda(b+j)\end{aligned}$$

where ka has been replaced by the new constant λ. By introducing these approximations into (2), we obtain

$$\begin{aligned}P(x;t)&=\frac{(x-1)!}{(x-b)!(b-1)!}\exp(-\lambda bt)\\ &\quad\times\sum_{j=0}^{x-b}\frac{(x-b)}{j!(x-b-j)!}\{-\exp(-\lambda t)\}^{j}\\ &=\binom{x-1}{x-b}\exp(-\lambda bt)\{1-\exp(-\lambda t)\}^{x-b} \qquad (3)\end{aligned}$$

in agreement with Delbrück's treatment.[4] He proposed the differential-difference equation (4) describing the statistical fluctuation of a simple autocatalytic reaction mechanism. We thus see that the probability distribution (3) satisfies the equation,

$$\frac{\mathrm{d}}{\mathrm{d}t}P(x;t)=\lambda(x-1)P(x-1;t)-\lambda xP(x;t) \qquad (4)$$

$$(x=b,\, b+1,\, \cdots)$$

on the assumption that the number of molecules of reactant A is so large that it remains constant through the course of reaction. As long as the initial number of molecules, a, is sufficiently large but finite, (3) is an approximation of (2) and holds only for the initial stage of the autocatalytic reaction. This will become still more clear by comparing the following two rate equations for the means $<x>$,

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}<x>&=k\{a-(<x>-b)\}<x>\\ &\quad-k(<x^2>-<x^2>)\end{aligned}$$

and

$$\frac{\mathrm{d}}{\mathrm{d}t}<x>=\lambda<x>$$

which can be derived from (1) and (4), respectively.

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