SIMULATION OF FIRST-ORDER CHEMICAL REACTION AS A STOCHASTIC PROCESS ON A DIGITAL COMPUTER

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Chemical reactions of first order (isolated, reversible or consecutive) are considered as simple birth and death processes. A random variable, a pseudorandom number in the interval (0,1), is attributed to the life time of a particle of reacting compound and the course of the reaction is simulated by generating these numbers on digital computer. The results illustrate the probability character of a chemical reaction in a system with a small number of particles and the difference between the stochastic and deterministic descriptions of the reaction course. It is shown how to use the simulation method in determining the mean number of particles.

A chemical reaction can be considered as a sequence of events governed by the laws of probability, *i.e.* as a stochastic process[1]. The stochastic theory of chemical reactions was worked out in detail recently[2,3]. Most papers deal with the calculation of the mean number of particles at time t and with the conditions at which the stochastic description of a reaction approaches the deterministic one given by the classical chemical kinetics. The principle of the stochastic method in chemical kinetics is the replacement of the deterministic continuous variable, concentration of particles at time t, by the probability that the number of particles of a given kind at time t is n. This number is considered as a random variable. Further, the transition probabilities in the system[2-4] or the probabilities of conversion for one particle[5,6] are postulated. From these postulates the distribution of the number of particles of a given kind, the mean value and fluctuation of the number of particles at time t can be derived.

The present communication deals with the stochastic model of first-order reactions which are considered as simple birth and death processes[1], and with the possibility of simulation of an idealized reaction course modelled as a stochastic process. By replacing the life time of a particle of the reacting compound by a new random variable, the problem is reduced to generation of pseudorandom numbers. The results illustrate the difference between the stochastic and classical deterministic description of a chemical reaction and make it clear that the irreproducibility of the time course of a reaction in a system with a small number of particles can be caused by the probability character of the process. In the case of an isolated first-order reaction, it is shown how the simulation method can be used to find the stochastic mean value of the number of particles of a given kind at time t.

Isolated First-Order Reaction A → B

We postulate: The probability that an arbitrary particle A will react in the interval $(t, t + \Delta t)$, where $\Delta t \to 0$, to give B is $k\,\Delta t$, where k is independent of time (*i.e.* the formation of the product B is considered as a pure birth process[1]). The conversion proper is instantaneous. This postulate implies: The probability that the particle A will not react in the mentioned interval is $1\text{-}k\,\Delta t$; the probability that it will not react in the finite interval $(0, t)$ ($t = 0$ denoting the beginning of the reaction) is the limit of $(1 - k\,\Delta t)^{t/\Delta t}$ for $\Delta t \to 0$, *i.e.* e^{-kt}; the probability that the particle A will not react in the same interval but will react in the interval $\langle t, t + \mathrm{d}t)$ (*i.e.* that its life time τ is in the interval $\langle t, t + \mathrm{d}t)$) is

$$\mathrm{Prob}\,\{t \leqq \tau < t + \mathrm{d}t\} = k\,\mathrm{e}^{-kt}\,\mathrm{d}t\,. \qquad (1)$$

The life time τ can be hence considered as a continuous random variable with a probability density $k\,\mathrm{e}^{-kt}$. We now introduce a new random variable

$$R = 1 - \mathrm{e}^{-k\tau}\,. \qquad (2)$$

Since $\tau \in (0, \infty)$, it follows $R \in (0, 1)$. This random variable is according to Eq. (*1*) subject to a uniform distribution with a unit probability density:

$$\mathrm{Prob}\,\{y \leqq R < y + \mathrm{d}y\} = \mathrm{d}y\,, \qquad (3)$$

where $y = 1 - \mathrm{e}^{-kt}$ is a real number in the interval $(0, 1)$. The random variable R will be represented by pseudorandom numbers in the interval $(0, 1)$ which are assumed to obey the distribution (*3*) (more precisely, their distribution is close to a quasi-uniform one). Such numbers can be generated on a digital computer[7]. Every generated number corresponds to a life time of one particle A according to Eq. (*2*). Provided that $N_A(0) = N$ denotes the initial number of particles A, the life time of all particles A can be obtained by generating N random numbers. If these are ordered in an increasing sequence, a stochastic time course of the reaction is obtained; by generating N random numbers R the course of the reaction A → B is simulated, *i.e.* an idealized experiment is made.

The system contains just $N - n$ particles A and n particles B at time t, if the life time of n particles A is shorter than t and that of $N - n$ particles A longer than t (*i.e.* if n generated numbers R_i are smaller and $N - n$ numbers R_i larger than $y = 1 - \mathrm{e}^{-kt}$, $i = 1, \ldots, N$). Hence

$$\mathrm{Prob}\,\{N_A(t) = N - n\} = \mathrm{Prob}\,\{N_B(t) = n\} =$$

$$= \binom{N}{n}\left[\mathrm{Prob}\,\{R_i < y\}\right]^n\left[\mathrm{Prob}\,\{R_i > y\}\right]^{N-n} = \binom{N}{n} y^n(1 - y)^{N-n}\,, \qquad (4)$$

where $N_X(t)$ denotes the number of particles X = A, B at time t and the expression on the right-hand side corresponds to the binomial distribution derived earlier[2,5] for a first-order reaction. The result can be interpreted also as follows: if M sets of N numbers R_i are generated, then of very large M all numbers R_i will fill up the interval (0,1) evenly and their number in the interval $(0, y)$ will approach MNy; their mean number in this interval corresponding to one set (one experiment) will be Ny in accord with the deterministic value of the number of particles B at time $tN(1 - e^{-kt})$. The most probable value of the n-th random number in the increasing series of N generated numbers is $(n - 1)/(N - 1)$ approaching n/N for N, $n \to \infty$. The most probable time, τ_n, in which the n-th particle reacts is given by

$$\tau_n = -k^{-1} \ln\left(1 - (n-1)/(N-1)\right) \xrightarrow{n,N\to\infty} -k^{-1} \ln\left(1 - n/N\right). \qquad (5)$$

The last term corresponds to the deterministic value of the time necessary to attain a conversion $x = n/N$.

Besides the described method of simulation of an isolated reaction of first order there is also another one, suitable even for more complicated reactions of first order. Again, a pseudorandom number $R \in (0, 1)$ corresponds to the life time of particle A according to Eq. (2). First, we generate N numbers $R_i^{(N)}$, $i = 1, \ldots, N$, select the smallest, $R_{\min}^{(N)}$, and attribute to one particle A the life time $\tau_1 = -k^{-1} \ln\left(1 - R_{\min}^{(N)}\right)$. The remaining $N - 1$ particles A are at the time τ_1 still

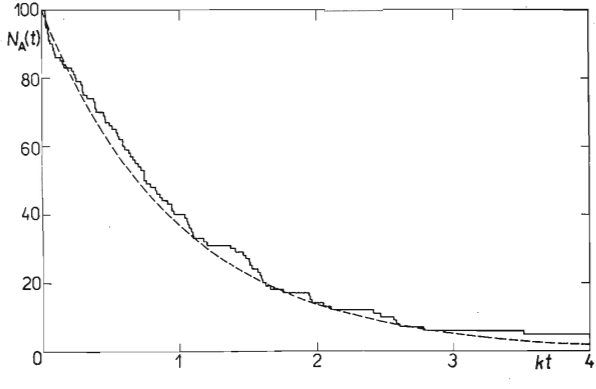

FIG. 1

Time Dependence of Number of Particles A for Reaction A → B
$N_A(0) = 100$.

in the state A. We now place the beginning of the time scale at the time τ_1 and follow the reaction in the system of $N - 1$ particles. We generate $N - 1$ new numbers $R_i^{(N-1)}$, $i = 1, \ldots, N - 1$, select the smallest, $R_{\min}^{(N-1)}$, and attribute to one of the $N - 1$ particles A a relative life time $\tau_2' = -k^{-1} \ln (1 - R_{\min}^{(N-1)})$; the life time of this particle in the original (laboratory) time scale is $\tau_2 = \tau_1 + \tau_2'$. Further we proceed analogously. The life time of the n-th reacting particle A in the original time scale is $\tau_n = \Sigma_1^n \tau_i'$. It can be proved that this method of calculation is equivalent to the preceding one; here also the probability that the system contains $N - n$ unreacted particles A at time t is given by the binomial distribution (*4*). The results of simulation of an isolated reaction of first order by the described method are shown in Fig. 1 for $N = 100$. The dashed curve corresponds to the deterministic solution for the number of particles A at time t, $N_A(t) = N e^{-kt}$, which is identical with the stochastic mean number of particles. For a great initial number of particles A, the statistically most probable time course approaches the deterministic curve.

Reversible First-Order Reaction $A \rightleftarrows B$

We postulate in this case: The probability that an arbitrarily chosen particle A will be converted to B in the time interval $(t, t + \Delta t)$, where $\Delta t \to 0$, is $k_1 \Delta t$; the probability that the particle B will be converted to A in the same time interval is $k_2 \Delta t$. The conversions are considered as instantaneous events. The numbers of particles A and B at time t are denoted as $N_A(t)$ and $N_B(t)$. The initial conditions are $N_A(0) = N$, $N_B(0) = 0$. The mentioned reaction was simulated by the described method, which was modified. At the beginning of the reaction ($t = 0$) the system contains $N_A(0) = N$ particles A. We generate N numbers $R_{A,i}^{(N)}$, $i = 1, \ldots, N$, select the smallest one, $R_{A,\min}^{(N)}$ and calculate the life time $\tau_1 = -k_1^{-1} \ln (1 - R_{A,\min}^{(N)})$ of one particle A.

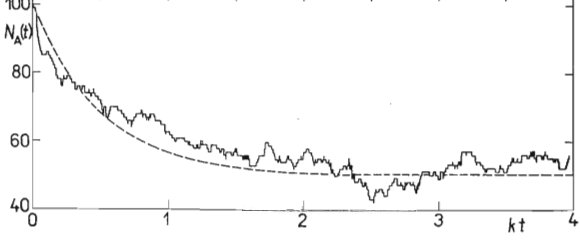

FIG. 2

Time Dependence of Number of Particles A for Reaction $A \rightleftarrows B$
$N_A(0) = 100$, $N_B(0) = 0$.

We choose a new time scale with the origin at τ_1 with respect to the original (laboratory) time scale. The system now contains $N - 1$ particles A and one particle B. We generate $N - 1$ numbers $R_{A,i}^{(N-1)}$, $i = 1, \ldots, N - 1$, and one number $R_{B,1}^{(1)}$, select the smallest number $R_{A,min}^{(N-1)}$ from the first group and calculate the life time of a particle A as $\tau_2' = -k_1^{-1} \ln (1 - R_{A,min}^{(N-1)})$ in the relative time scale. The number $R_{B,1}^{(1)}$ corresponds to the life time of a particle B, $\tau_2'' = -k_2^{-1} \ln (1 - R_{B,1}^{(1)})$ in the relative time scale. If $\tau_2' < \tau_2''$, another particle A will react at time $\tau_2 = \tau_1 + \tau_2'$; if $\tau_2' > \tau_2''$, the particle B will be converted to A at time $\tau_2 = \tau_1 + \tau_2''$. Generally, when the system contains $N - n$ particles A and n particles B, we generate $N - n$ numbers $R_{A,i}^{(N-n)}$ and n numbers $R_{B,i}^{(n)}$, select in both groups the smallest one and calculate the corresponding relative life times, of which the smaller one gives the time in which the particle A (for $R_{A,min}^{(N-n)} < 1 - (1 - R_{B,min}^{(n)})^{k_1/k_2}$) or B (for $R_{A,min}^{(N-n)} > 1 - (1 - R_{B,min}^{(n)})^{k_1/k_2}$) reacts. On returning to the original time scale, we obtain the course of the reaction. The results of this calculation are shown in Fig. 2 for $N = 100$ and $k_1 = k_2$. The dashed curve shows the deterministic solution and the stochastic mean. The fluctuation of the system near to equilibrium is also illustrated.

Consecutive First-Order Reactions $A \rightarrow B \rightarrow C$

We postulate analogously that the probability of conversion of a particle A to B in the time interval $(t, t + \Delta t)$, where $\Delta t \rightarrow 0$, is $k_1 \Delta t$, and the probability of conver-

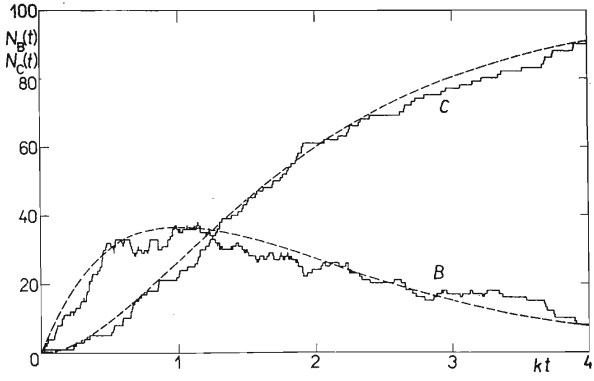

FIG. 3

Time Dependence of Numbers of Particles B and C for Reaction $A \rightarrow B \rightarrow C$
$N_A(0) = 100$, $N_B(0) = N_C(0) = 0$.

sion of B to C in the same time interval is $k_2 \Delta t$. The system contains at the beginning N particles A and none B or C. The method of simulation of this reaction is analogous to the preceding one: When the system contains m particles A and n particles B $(m + n \leqq N)$, we generate m numbers $R_{A,i}^{(m)}$, $i = 1, \ldots, m$, and n numbers $R_{B,i}^{(n)}$, $i = 1, \ldots, n$, select the smallest one in both groups and calculate the corresponding life times of which the smaller one gives the time in which the particle A will be converted to B or B to C. On returning to the laboratory time scale, we gradually obtain the course of the reaction. Again, it can be shown that this method yields the same probability relations as the usual stochastic treatment. The results of simulation of the considered reaction for $N = 100$ and $k_1 = k_2$ are shown in Fig. 3; the dashed curve corresponds to the deterministic solution, which is identical with the stochastic mean.

The described method of simulation of first-order reactions can be used to determine the mean number of particles of a given kind at time t. The simulation of the reaction

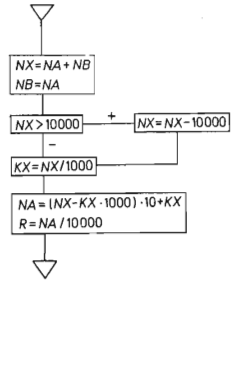

FIG. 4

Block Diagram of Algorithm for Generating Pseudorandom Numbers

NA and *NB* denote arbitrary four-digit positive integers, *KX* positive integer formed by dropping all digits after decimal point, *R* pseudorandom number with four significant digits.

TABLE I

Results of Testing Generated Pseudorandom Numbers

NA and *NB* are arbitrary four-digit positive integers, $\langle R \rangle$ mean value of pseudorandom number calculated from 10 000 generated numbers corresponding to *NA* and *NB*, and $\langle R^2 \rangle$ the corresponding mean square value.

NA	*NB*	$\langle R \rangle$	$\langle R^2 \rangle$
3 194	2 744	0·4974	0·3296
6 214	5 807	0·5015	0·3354
8 537	4 069	0·4966	0·3303

represents an idealized experiment. If a large number of simulations for a given system is carried out (hence a large number of experiments), the number of particles of a given kind at time t obtained by averaging over all simulations (experiments) will approach with increasing number of simulations the stochastic mean number of particles at time t.

Algorithm for Generating Pseudorandom Numbers

Pseudorandom numbers in the interval (0,1) with four significant figures were generated with the aid of an algorithm described by the block diagram in Fig. 4.* Testing of 10 000 generated numbers gave for various values of NA and NB the results shown in Table I. No period was found during generating the numbers. The simulation and testing were performed on a Hewlett-Packard 2116 B computer and the program was written in Fortran II.

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* This algorithm is a modification of the additive congruential pseudorandom number generator.