SIMULATION OF STOCHASTIC MODELS OF HIGHER-ORDER REACTIONS

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A simulation method to obtain stochastic models of bimolecular reactions of the type $A + B \rightarrow P$ or $A + B \rightleftarrows P + Q$ and an autocatalytic reaction of the type $A \rightarrow P$, $A + P \rightarrow 2P$ is proposed. This method is used to study fluctuations in the composition of a system with a reversible bimolecular reaction close to equilibrium and to calculate the mean number and variance of the number of product particles in the case of an autocatalytic reaction.

According to the stochastic theory[1,2], a chemical reaction represents a sequence of reaction events (conversions of the individual particles of the starting substances to products and *vice versa*), for which the elementary infinitesimal probabilities can be postulated. Based on the probability model, the reaction course can be simulated on a digital computer. We showed in previous communications[3,4] how the course of simple first-order reactions can be simulated and we used the simulation method to study the fluctuations of the system's composition close to equilibrium. Now we shall show how the simulation method can be formulated for higher-order reactions, namely an irreversible bimolecular reaction, $A + B \rightarrow P$, an autocatalytic reaction, $A \rightarrow P$, $A + P \rightarrow 2P$, and a reversible bimolecular reaction, $A + B \rightleftarrows P + Q$.

Reaction Model

We shall consider a closed system of unit volume, in which one of the envisaged reactions proceeds at constant temperature (*i.e.*, the system is in contact with a large heat reservoir of a constant temperature). The number of particles $X = A, B, P,$ or Q at a time t is denoted as $N_X(t)$. At the beginning, $t = 0$, the system contains only particles of the starting substances, *i.e.*, $N_A(0) = N_A^0, N_B(0) = N_B^0, N_P^0 = N_Q^0 = 0$; for the sake of simplicity $N_A^0 = N_B^0 = N$. The state of the system is characterized by the number of particles P, $N_P(t)$. The probability that in the system, which is at a time t in the state $N_P(t) = j$, an arbitrary particle or a pair of particles of the starting substances is changed into products in the interval $(t, t + \Delta t)$, $\Delta t \rightarrow 0$, is according to the postulate of the stochastic theory[1,2] equal to $r_j \Delta t$; the probability that in the

same interval an arbitrary particle or a pair of particles of the products is changed into the starting substances is $r'_j \Delta t$. Further it follows from the postulates of the theory that $r_j = k(N - j)^2$, $r'_j = 0$ for the reaction $A + B \rightarrow P$, $r_j = (N - j) \cdot (k_1 + k_2 j)$, $r'_j = 0$ for the reaction $A \rightarrow P$, $A + P \rightarrow 2 P$, and $r_j = k_3(N - j)^2$, $r'_j = k_4 j^2$ for $A + B \rightleftarrows P + Q$. According to the assumptions of the theory, the constants k, k_1, k_2, k_3 and k_4 are independent of time.

Simulation of Reactions

The system, which passed into a state j at a time t, passes at a time $t + \tau_j$ into some neighbouring state (in the case of an irreversible reaction into a state $j + 1$, in the case of a reversible reaction into $j + 1$ or $j - 1$). The quantity τ_j, which can be interpreted as the life time of the state j, represents a random variable that can attain any value in the interval $(0, \infty)$. It follows from the postulated probabilities of the elementary conversions that

$$\text{Prob}\left\{\tau \leqq \tau_j < \tau + d\tau\right\} = (r_j + r'_j) \exp\left[-(r_j + r'_j)\tau\right] d\tau . \qquad (1)$$

We assign to the quantity τ_j a new random variable X_j by the relation

$$X_j = 1 - \exp\left[-(r_j + r'_j)\tau_j\right]. \qquad (2)$$

It is obvious that $X_j \in (0, 1)$ and that

$$\text{Prob}\left\{x \leqq X_j < x + dx\right\} = \text{Prob}\left\{\tau \leqq \tau_j < \tau + d\tau\right\} = dx , \qquad (3)$$

where $x = 1 - \exp\left[-(r_j + r'_j)\tau\right]$. The quantity X_j has therefore in the interval $(0, 1)$ a unit probability density and represents a random number. Random (more precisely, pseudorandom) numbers can be generated on a digital computer by means of a previously described algorithm[3].

In the case of an irreversible bimolecular or autocatalytic reaction, the reaction course can be simulated with the use of generated random numbers as follows: We generate in turn numbers X_0, X_1, X_2, ..., X_N and from the relation

$$\tau_j = -\ln\left(1 - X_j\right)/r_j, \quad j = 0, 1, 2, , ..., N , \qquad (4)$$

obtain the life times of the states $N_P(t) = 0, 1, 2, ..., N$. The time in which the j-th particle P is formed is equal to $\sum_{i=0}^{j} \tau_i$. In this way we obtain an overall picture of the reaction course.

In the case of a reversible bimolecular reaction, generating of a single random number for one reaction event enables to determine only the life time of a given state but not the state into which the system shall pass. The probability that the system which is in a state j passes by a subsequent reaction event into a state $j + 1$ is

$$p_{j,j+1} = k_3(N - j)^2 / [k_3(N - j)^2 + k_4 j^2],\qquad(5)$$

and the probability that it passes into a state $j - 1$ is

$$p_{j,j-1} = 1 - p_{j,j+1} = k_4 j^2 / [k_3(N - j)^2 + k_4 j^2].\qquad(6)$$

We therefore generate for every reaction event a second random number $Y_j \in (0, 1)$. If $Y_j < p_{j,j+1}$, the passage $j \to j + 1$ occurs; if $Y_j > p_{j,j+1}$, the passage $j \to j - 1$ occurs. By generating in turn pairs of random numbers X_j, Y_j, the reaction course in the time scale can be simulated.

Similarly as in the case of a reversible unimolecular reaction[4], it is possible to study by the simulation method fluctuations in the system's composition close to the equilibrium of the reaction $A + B \rightleftarrows P + Q$. In this case it is sufficient to follow
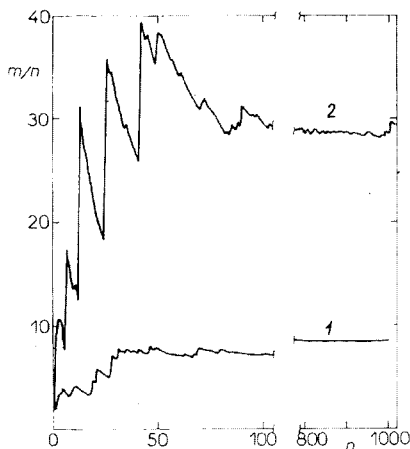

FIG. 1

Mean Number of Reaction Events between Returns into State $N/2$ for a System with Reaction $A + B \rightleftarrows P + Q$
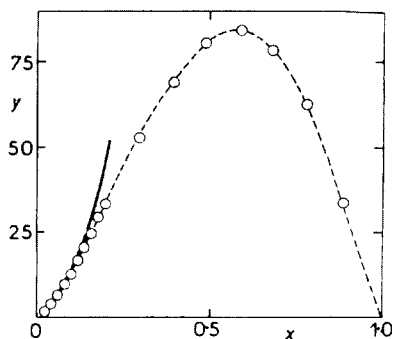*1* $N = 100$; *2* $N = 1000$.

FIG. 2

Variance of the Number of Particles P for Autocatalytic Reaction
$y = D^2\{N_P(t)\}$, $x = \langle N_P(t)\rangle/N$, $N = 50$, $k_1 = 0.01\ \mathrm{s}^{-1}$, $k_2 = 0.004\ \mathrm{s}^{-1}$. Solid line corresponds to Eq. (8), points to simulated data.

the fluctuations in the number of reaction events scale (for the mathematical description of the probability model of this reaction in the number of events scale see[5]). For the sake of simplicity, we set $k_3 = k_4$ and assume N even. Since we follow the reaction in the scale of reaction events, it is sufficient to generate for every event a single random number, Y_j, which determines the type of the transition from a state j. If we choose as the starting state $N_A(0) = N_B(0) = N_P(0) = N_Q(0) = N/2$ (i.e., a state corresponding to the deterministic equilibrium), it is possible to follow the number of reaction events between returns into the state $N/2$. The mean number of events between returns into this state derived from the theory[5] is

$$\mu_{N/2} \approx \tfrac{1}{2}(\pi N)^{1/2} . \tag{7}$$

A simulation gives the dependence of the ratio of the number of events, m, to the number of returns into the state $N/2$, n, on the number of returns. Such a simulation was performed for $N = 100$ $(\mu_{50} \approx 8.85)$ and $N = 1000$ $(\mu_{500} \approx 28)$. The ratio m/n approaches with increasing n the theoretical value $\mu_{N/2}$ as shown in Fig. 1.

The proposed simulation method was used by us to study autocatalytic reactions of the type $A \rightarrow P$, $A + P \rightarrow 2P$, for which a formula for the variance of the number

TABLE I

Mean Degrees of Conversion of Substance A ($N = 50$, $k_1 = 0.01\ \text{s}^{-1}$)

x_{det}	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
x_{sim}, $k_2 = 0.004\ \text{s}^{-1}$	0·099	0·195	0·287	0·376	0·462	0·554	0·646	0·745	0·850
x_{sim}, $k_2 = 0.020\ \text{s}^{-1}$	0·090	0·164	0·229	0·292	0·352	0·418	0·489	0·565	0·666

TABLE II

Mean Degrees of Conversion of Substance A and Variances of the Number of Particles P ($N = 20$, $k_1 = 0.01\ \text{s}^{-1}$, $k_2 = 0.004\ \text{s}^{-1}$)

x_{det}	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
x_{stoch}[a]	0·0978	0·192	0·282	0·371	0·459	0·549	0·642	0·741	0·853
x_{sim}	0·0981	0·192	0·280	0·369	0·455	0·543	0·635	0·729	0·829
$D^2_{stoch}\{N_P\}$[a]	2·95	6·81	10·6	13·6	15·6	16·3	15·4	12·6	7·39
$D^2_{sim}\{N_P\}$	3·09	6·87	10·5	13·2	15·2	15·8	14·2	11·6	6·59

[a] Index stoch denotes exact stochastic values calculated from the known distribution[6] of the number of particles P at a time t.

of particles P, $D^2\{N_P(t)\}$, was derived earlier[6] by an approximate method. The mean value and variance of the number of particles P were calculated as mean values from 1 000 simulations (*i.e.*, idealized experiments). Fig. 2 shows the variance of the number of particles P thus determined together with values calculated from the approximate formula[6]

$$D^2\{N_P(t)\} = \langle N_P(t) \rangle + (k_2/k_1) \langle N_P(t) \rangle^2 , \qquad (8)$$

where $\langle N_P(t) \rangle$ means stochastic mean number of particles P, for $N = 50, k_1 = 0.01 \text{ s}^{-1}$ and $k_2 = 0.004 \text{ s}^{-1}$ $(k_1/k_2 = 2.5)$. By comparison it follows that Eq. (8) gives results close to the simulated values only for a low degree of conversion $x = \langle N_P(t) \rangle / N$. The variance is a maximum for $x \approx 0.6$.

Simulated mean values of the degree of conversion x_{sim}, at a time t corresponding to the given deterministic degree of conversion, x_{det} $(= N_P^{det}/N$, where N_P^{det} denotes deterministic number of particles P at a time $t)$, are given in Table I. The values of x_{sim} are considerably lower than x_{det}. However, a comparison of the simulated mean values and variances with exact stochastic values for $N = 50$ was not possible (for difficulties in numerical calculations), therefore we carried out another 1 000 simulations for $N = 20$. In this case it is possible to obtain the first and second moments directly by a numerical calculation from the distribution of the number of particles P at a time t, which was derived previously[6]. The results are given in Table II. The simulated and exact mean values of the degree of conversion are practically identical (maximum deviation 3%). Larger differences are in the variances (maximum deviation 10%). It can be therefore expected that for $N = 50$ the values of x_{sim} obtained from 1 000 simulations would be also close to the exact stochastic mean values.

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