ALTERNATIVE STOCHASTIC FORMULATION OF FIRST-ORDER REACTION KINETICS

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A stochastic description of the kinetics of some reactions of first order (consecutive irreversible, reversible, and parallel irreversible reactions) is derived. The method eliminates the necessity of solving differential-difference equations and is based on determining the probability of transformation of one particle in a finite time interval.

The stochastic concept has been applied in the description of a number of mono- and bimolecular reactions[1]. For the studied types of first-order reactions (isolated[2,3], reversible[3] and two parallel reactions[3], multicomponent system of first-order reactions[4], triangular reaction[5]), it was shown that an exact solution can be found for the mean number of particles of a given type at time t and for fluctuation of the number of particles; the stochastic mean number of particles agrees with classical (deterministic) value. In most cases[1,3,4], the system was described by a system of differential-difference equations which were solved with the aid of a generating function.

In the present paper the stochastic concept is applied to the kinetics of consecutive irreversible reactions, a reversible and a parallel irreversible one, all of first order, hence cases solved already earlier[1,3,4]. However, the method of solution is different in that it is simpler and avoids the solution of differential-difference equations.

Consecutive Irreversible First-Order Reactions

We shall consider j-1 consecutive irreversible reactions of first order:

$$A_i \rightarrow A_{i+1}\,, \quad i = 1\,, \ldots j\text{-}1\,. \qquad (1)$$

Let the number of particles A_i at time t be $N_{A_i}(t)$; we assume that $N_{A_1}(0) = N$ and $N_{A_i}(0) = 0$ for $i > 1$. Further, the probability that the particle A_i will be transformed to A_{i+1} during a very short time interval $\Delta t(\Delta t \rightarrow 0)$ is $k_i\,\Delta t$. The conversion of A_i to A_{i+1} is considered as an instantaneous event (this assumption is discussed elsewhere[6]). The system (*1*) will be described stochastically if the probability $P_n^{(A_i)}(t)$ that the number of particles A_i at time t is n $(i = 1, \ldots j,\ n = 0,1 \ldots N)$ is known at any time $t > 0$. Let $p_i(t)$ be the probability that an arbitrarily selected particle A_1

will be converted to A_i during the time interval (0, t), then $P_n^{(A_i)}(t)$ can be derived as follows: The system will contain just n particles A_i at time t if n particles A_1 were converted to A_i in the interval $(0, t)$ and N-n particles A_1 were converted to A_r $(r \neq i)$ or did not react at all. The probability that n selected particles A_1 were converted to A_i is $p_i^n(t)$ and the probability that the remaining $N-n$ particles A_1 did not react, or were converted to A_r $(r \neq i)$ is $[1 - p_i(t)]^{N-n}$. There are $\binom{N}{n}$ possibilities how to divide N numbered particles into two groups containing n and $N-n$ particles. Since it plays no role what particles A_1 were converted to A_i but only their number is important, we have

$$P_n^{(A_i)}(t) = \binom{N}{n} p_i^n(t) \left[1 - p_i(t)\right]^{N-n} . \tag{2}$$

These probabilities correspond to the binomial distribution and fulfil the relation

$$\sum_{n=0}^{N} P_n^{(A_i)}(t) = 1 . \tag{2a}$$

Assuming that the particle A_i will be changed to A_{j+1} in a very short time interval Δt with the probability $k_i \, \Delta t$, we can derive $p_i(t)$ in the integral form. For $i = 1$:

$$p_1(t) = \lim_{\Delta t \to 0} (1 - k_1 \, \Delta t)^{t/\Delta t} = \exp(-k_1 t) , \tag{3}$$

which means the probability that the particle A_1 did not react in the interval $(0, t)$. For $i = 2, \dots j$:

$$p_i(t) = k_1 \dots k_{i-1} \int_{\tau_{i-1}=0}^{t} \int_{\tau_{i-2}=0}^{\tau_{i-1}} \dots \int_{\tau_1=0}^{\tau_2} \exp\left[-k_1\tau_1 - k_2(\tau_2 - \tau_1) - \dots \right.$$
$$\left. - k_{i-1}(\tau_{i-1} - \tau_{i-2}) - k_i(t - \tau_{i-1})\right] d\tau_1 \dots d\tau_{i-1} . \tag{4}$$

Here τ_r $(r = 1, \dots i - 1)$ are auxiliary integration variables denoting time in which the particle A_r is changed to A_{r+1}; for $i = j$ we set $k_j = 0$.

The mean number of particles A_i at time t, $\langle N_{A_i}(t)\rangle$, is for the binomial distribution (2) given by

$$\langle N_{A_i}(t)\rangle = \sum_{n=0}^{N} n P_n^{(A_i)}(t) = N p_i(t) . \tag{5}$$

With the use of Eqs (3) and (4) it can be shown that this mean value fulfils the relation

$$d\langle N_{A_i}(t)\rangle/dt = N \, dp_i(t)/dt = - N k_i p_i(t) + N k_{i-1} p_{i-1}(t) =$$
$$= - k_i \langle N_{A_i}(t)\rangle + k_{i-1}\langle N_{A_{i-1}}(t)\rangle , \tag{6}$$

which is analogous to the law of mass action in classical chemical kinetics. Eqs (*6*) for $i = 1, \ldots j$ ($k_0 = k_j = 0$) form a system of linear differential equations of first order which, together with the initial conditions $N_{A_i}(0) = N\delta_{1i}$ for $i = 1, \ldots j$, is identical with the set of equations describing the reacting system in a deterministic way and has therefore the same solution.

The coefficient of variation (relative fluctuation) of the number of particles for the distribution (*2*) is given as

$$CV\{N_{A_i}(t)\} \equiv (\langle N_{A_i}^2(t)\rangle - \langle N_{A_i}(t)\rangle^2)^{1/2}/\langle (N_{A_i}(t)\rangle =$$

$$= \{[p_i^{-1}(t) - 1]/N\}^{1/2} = (\langle N_{A_i}(t)\rangle^{-1} - N^{-1})^{1/2} . \qquad (7)$$

The mean time, T_i, of the conversion of A_1 to A_i is given as

$$T_i = \int_0^\infty k_{i-1} t p_{i-1}(t)\, dt , \quad i = 2, \ldots j . \qquad (8)$$

From the Eqs (*6*) and (*8*) we obtain the recurrent formula

$$T_i = T_{i-1} + \int_0^\infty p_{i-1}(t)\, dt . \qquad (9)$$

The latter integral can be determined in the following way. From Eq. (*6*) it follows

$$k_i \int_0^\infty p_i(t)\, dt = k_{i-1} \int_0^\infty p_{i-1}(t)\, dt - [p_i(t)]_0^\infty . \qquad (10)$$

Here the last term is equal to zero for $1 < i < j$. Since $\int_0^\infty p_1(t)\, dt = 1/k_1$, it follows from this equation that $\int_0^\infty p_i(t)\, dt = 1/k_i$. The mean time of conversion of A_1 to A_2 is $T_2 = \int_0^\infty \exp(-k_1 t)\, k_1 t\, dt = 1/k_1$. Therefore, from Eq. (*9*) we obtain

$$T_i = \sum_{r=1}^{i=1} 1/k_r . \qquad (11)$$

If one of the values of k_r ($r = 1 \ldots j - 1$) is much smaller than the others, *e.g.* k_s, then $T_j \approx 1/k_s$. The conversion of A_s to A_{s+1} is then the rate-determining step in reaction (*1*).

Reversible First-Order Reaction

We shall consider a reversible reaction of the type

$$A \rightleftarrows B . \qquad (12)$$

Let the number of particles A and B at time $t = 0$ be N and zero, respectively. Further, let the probability that the particle A will react in a very short time interval Δt to form B be $k_1 \Delta t$ and the probability that the particle B will be converted to A during this time interval be $k_2 \Delta t$. Both conversions proper, A → B and B → A, are considered as instantaneous events.

The probability $p_A(t)$ that a selected particle A will not be changed to B at time t (regardless to whether it remains in the interval $(0, t)$ in the form A or not) is

$$p_A(t) = \exp(-k_1 t) \{1 + \sum_{m=1}^{\infty} (k_1 k_2)^m \, . \int_{\tau_{2m}=0}^{t} \int_{\tau_{2m-1}=0}^{\tau_{2m}} \dots \int_{\tau_1=0}^{\tau_2} \exp[\sum_{i=1}^{2m} (-1)^i (k_1 - k_2) \tau_i] \, d\tau_1 \dots d\tau_{2m}\} \, . \quad (13)$$

The probability $p_B(t)$ that an arbitrarily selected particle A will be converted to B at time t is

$$p_B(t) = k_1 \exp(-k_2 t) \sum_{m=0}^{\infty} (k_1 k_2)^m \, . \int_{\tau_{2m+1}=0}^{t} \int_{\tau_{2m}=0}^{\tau_{2m+1}} \dots \int_{\tau_1=0}^{\tau_2} \exp[\sum_{i=1}^{2m+1} (-1)^i (k_1 - k_2) \tau_i] \, d\tau_1 \dots d\tau_{2m+1} \, . \quad (14)$$

The auxiliary variables τ_i in Eqs (*13*) and (*14*) denote time in which A was changed to B (i is odd) or B to A (i is even). From Eqs (*13*) and (*14*) we obtain a differential equation for $p_B(t)$:

$$dp_B(t)/dt = -k_2 p_B(t) + k_1[1 - p_B(t)] \, . \quad (15)$$

Its initial condition is $p_B(0) = 0$; its solution is

$$p_B(t) = k_1\{1 - \exp[-(k_1 + k_2) t]\}/(k_1 + k_2) \, . \quad (16)$$

Since $p_A(t) + p_B(t) = 1$,

$$p_A(t) = \{k_2 + k_1 \exp[-(k_1 + k_2) t]\}/(k_1 + k_2) \, . \quad (17)$$

The probability that the system contains n particles X at time t, $P_n^{(X)}(t)$, is equal to the product of both probabilities that n particles A are in the state X at time t and that $N - n$ particles A are not in the state X at time t, multiplied by the number of possible arrangements of N numbered particles into two groups containing n and $N - n$ particles:

$$P_n^{(X)}(t) = \binom{N}{n} p_X^n(t) \left[1 - p_X(t)\right]^{N-n} ; \quad X = A \text{ or } B , \quad n = 0,1 \dots N . \tag{18}$$

This equation corresponds again to a binomial distribution. The mean number of particles X in the system, $\langle N_X(t) \rangle$, is

$$\langle N_X(t) \rangle = N p_X(t) ; \quad X = A \text{ or } B . \tag{19}$$

Eqs (*16*), (*17*) and (*19*) are in accord with the deterministic solution. The coefficient of variation of the number of particles in the system is

$$CV\{N_X(t)\} = \{[p_X^{-1}(t) - 1]/N\}^{1/2} ; \quad X = A \text{ or } B . \tag{20}$$

For $t \to \infty$ (thermodynamic equilibrium) we have

$$\lim_{t \to \infty} P_n^{(A)}(t) = \binom{N}{n} k_1^{N-n} k_2^n / (k_1 + k_2)^N = \binom{N}{n} K^{N-n} / (1 + K)^N , \tag{21a}$$

$$\lim_{t \to \infty} P_n^{(B)}(t) = \binom{N}{n} k_1^n k_2^{N-n} / (k_1 + k_2)^N = \binom{N}{n} K^n / (1 + K)^N , \tag{21b}$$

where $K = k_1/k_2$ is the equilibrium constant of the reaction. Further,

$$\lim_{t \to \infty} \langle N_A(t) \rangle = N k_2 / (k_1 + k_2) = N/(1 + K) , \tag{22a}$$

$$\lim_{t \to \infty} \langle N_B(t) \rangle = N k_1 / (k_1 + k_2) = NK/(1 + K) . \tag{22b}$$

The coefficient of variation is:

$$\lim_{t \to \infty} CV\{N_A(t)\} = (K/N)^{1/2} , \tag{23a}$$

$$\lim_{t \to \infty} CV\{N_B(t)\} = (1/KN)^{1/2} . \tag{23b}$$

These limiting relations correspond to equations derived for mean values and fluctuations of the number of particles in statistical thermodynamics[7].

Irreversible Parallel Reactions

We shall consider j parallel irreversible reactions of first order:

$$A_0 \to A_i ; \quad i = 1, \dots j , \tag{24}$$

and assume that the number of particles A_0 at time $t = 0$ is $N_{A_0}(0) = N$ and the number of particles A_i at time $t = 0$ is $N_{A_i}(0) = 0$ for $i = 1, \dots j$. Let the probability that the particle A_0 will react in a very short time interval $\Delta t \to 0$ to form A_i be $k_i \Delta t$. Then the probability $p_0(t)$ that a selected particle A_0 will not react during the time interval $(0, t)$ is

$$p_0(t) = \lim_{\Delta t \to 0} (1 - \sum_{i=1}^{j} k_i \Delta t)^{t/\Delta t} = \exp(-\sum_{i=1}^{j} k_i t), \quad (25)$$

and the probability $p_i(t)$ that a selected molecule A_0 will react during the interval $(0, t)$ to form A_i is

$$p_i(t) = \int_0^t \exp(-\sum_{i=1}^{j} k_i \tau) k_i \, d\tau = (k_i / \sum_{i=1}^{j} k_i) \cdot [1 - \exp(-\sum_{i=1}^{j} k_i t)]; \quad i = 1, \dots j. \quad (26)$$

The sum of all probabilities p_i $(i = 0, 1, \dots j)$ is equal to 1. The probability $P_n^{(A_i)}(t)$ that the system contains n particles A_i at time t $(i = 0, 1, \dots j)$ is again given by the binomial distribution

$$P_n^{(A_i)}(t) = \binom{N}{n} p_i^n(t) [1 - p_i(t)]^{N-n}; \quad i = 0, 1, \dots j. \quad (27)$$

The mean number of particles A_i and coefficient of variation of the number of particles are given by analogous expressions as in the preceding cases:

$$\langle N_{A_i}(t) \rangle = N p_i(t), \quad i = 0, 1, \dots j, \quad (28)$$

$$CV\{N_{A_i}(t)\} = \{[p_i^{-1}(t) - 1]/N\}^{1/2}; \quad i = 0, 1, \dots j. \quad (29)$$

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