The Stochastic Model for Unimolecular Gas Reaction

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According to the probabilistic representation for the deterministic theory of the "true" unimolecular gas reaction[1], in which it is assumed that the reactant molecules are independent of the coexisting resultant molecules, i. e., the distribution of each reactant molecule is not correlated to the distribution of each resultant molecule, and that the reverse reaction is not taking place, the fraction of the reactant molecules which react during time dt can be set equal to the probability k_1dt;

$$-\frac{\mathrm{d}n}{n}=k_1\mathrm{d}t \qquad (1)$$

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[1] Jen-Yuan Chien, *J. Chem. Phys.*, **16**, 426 (1948). See, e. g., A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", John Wiley & Sons, Inc., New York (1953), p. 67.

where the rate constant k_1 denotes the probability that one molecule reacts during unit time, n is the number of reactant molecules at time t and $-\mathrm{d}n$ the number reacting during time $\mathrm{d}t$. It should be emphasized, however, that in Eq. 1 the probabilistic notions are not manifested in a precise form, and that the number of molecules predicted for various times is not precise, but the reaction proceeds at random at an average rate[2]. In order to formulate this on the basis of the mathematically exact laws of the theory of probability, Bartholomay[3] has recently presented a method to construct the stochastic model for the true unimolecular gas reaction by starting from the deterministic theory as represented by Eq. 1. But the chemical and mathematical foundations on which the theory of the stochastic process can be applied to this chemical reaction do not appear to have been exactly mentioned. Therefore it is instructive to formulate definitely the probabilistic properties of the chemical reaction.

If the number of resultant molecules produced during the time interval $(0, t)$ is denoted by $n_p(t)$, the function $n_p(t)$ itself is a random variable for all arbitrary but fixed periods of duration t. Since the function $n_p(t)$ which assumes only the integers and is nondecreasing becomes the aggregate of random variables with continuous parameter when t varies, this represents a possible development of the chemical reaction. Consequently the course of the chemical reaction is a stochastic process. It has been acknowledged, in general, that under the given temperature and external parameters the rate of a chemical reaction is determined only by the composition of the reaction system at the time and does not depend on its previous history, so that it is concluded that the course of chemical reaction is a Markov process[4]. It has been recognized for many years that by its very nature a chemical reaction must disturb the equilibrium distribution of the reactant species[5]. If, however, we assume that the rate of the chemical reaction is sufficiently small compared with the rate of energy exchange and the disturbance of the equilibrium distribution of energy during the course of the chemical reaction can be approximately neglected, the reaction system can be discussed on the assumption that it is at thermal equilibrium. By " temporally homogeneous "[6] for the course of chemical reaction we mean that the thermal equilibrium remains absolutely unchanged throughout the process. Accordingly, we obtain the conclusion that *the theory of temporally homogeneous Markov process can be applied to the course of chemical reaction* for such reaction systems at thermal equilibrium that the reactant molecules do not interact mutually with the coexisting resultant molecules and the reverse reaction does not occur, and such conditions permit us to calculated the average rate of the chemical reaction at a time.

Although the one-dimensional stochastic process for the total number of reactant molecules has been studied by Bartholomay who, from the macroscopic point of view, has given a rate constant to the whole reaction, we shall be able to calculate the average rate constant by constructing microscopically the multi-dimensional stochastic process[7] for the number of reactant molecules in various states of energy, on the assumption that the stochastic model is conformable also to the " true " unimolecular reaction concerning the reactant molecules in each state of energy.

One-dimensional Stochastic Model

In general the Chapman-Kolmogorov equation for temporally homogeneous Markov processes[8] is given by

$$P_{i,n}(t+\tau)=\sum_{\nu}P_{i,\nu}(t)\cdot P_{\nu,n}(\tau) \tag{2}$$

where $P_{i,\nu}(t)$ is the transition probability from any state E_i to any other state E_ν during the time interval of length t and for the process of chemical reaction i, ν and n represent the numbers of reactant molecules, respectively. If the initial probability $P_i(0)$ is known, then the probability $P_n(t)$ of finding the system at time t in the state E_n is set equal to the quantity $\sum_{i=0}^{n_0}P_i(0)P_{i,n}(t)$ according to the theorem of total probability[9], that is, $P_n(t)=\sum_{i=0}^{n_0}P_i(0)P_{i,n}(t)$, where n_0 is the total number of reactant molecules at time $t=0$. Hence this probability $P_n(t)$ is related to both t and $P_i(0)$. In our case, however, it may be provided that one of the probabilities $P_i(0)$ $(i=0, 1, 2, \cdots\cdots, n_0)$ is equal to one, and the others to zero;

$$\text{if} \qquad i=n_0, \quad P_i(0)=1 \tag{3}$$

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[2] L. Pauling, " General Chemistry ", W. H. Freeman and Co. (1949), p. 335.

[3] G. F. Bartholomay, *Bull. Math. Biophys.*, **20**, 175 (1958).

[4] W. Feller, " An Introduction to Probability Theory and its Applications ", John Wiley & Sons, Inc., New York (1950), p. 337.

[5] R. H. Fowler and E. A. Guggenheim, " Statistical Thermodynamics ". Cambridge University Press (1939), p. 490.

[6] W. Feller, Ref. 4, p. 386.

[7] N. Arley, " On the Theory of Stochastic Process and their Application to the Theory of Cosmic Radiation ", John Wiley & Sons, Inc., New York (1948), p. 73.

[8] W. Feller's book, p. 388.

[9] A. N. Kolmogorov. " Foundations of the Theory of Probability " (Translation edited by Nathan Morrison), Chelsea Publishing Co., New York (1950). p. 7.

otherwise, $P_i(0)=0$

Multiplying both sides of Eq. 2 by $P_i(0)$ and summing over all values of i, we get

$$\sum_{i=0}^{n_0} P_i(0)P_{i,n}(t+\tau)=\sum_{\nu}\Big(\sum_{i=0}^{n_0} P_i(0)P_{i,\nu}(t)\Big)P_{\nu,n}(\tau)$$

which is reduced to, according to the theorem of total probability,

$$P_n(t+\tau)=\sum_{\nu} P_\nu(t)P_{\nu,n}(\tau) \tag{4}$$

where $P_\nu(t)$ denotes the probability of finding ν reactant molecules at time t in the reaction system. This is the fundamental equation for the application of the stochastic process to the chemical reaction.

If at time t the reaction system is in the state E_n, the probability that any one of n reactant molecules will undergo a reaction during the infinitely small time interval of length $(t, t+\tau)$ is equal to $P_{n,n-1}(\tau)=k_1 n\tau+o(\tau)$, where k_1 is a constant and $o(\tau)$ denotes the probability that more than one reaction occurs is of smaller order of magnitude than τ. Similarly the transition probability $P_{n+1,n}(\tau)$ from the state E_{n+1} to the adjacent state E_n is equal to $k_1(n+1)\tau+o(\tau)$, and the probability of staying in the state E_n is given by $P_{n,n}(\tau)=1-P_{n,n-1}(\tau)=1-(k_1 n\tau+o(\tau))$. Rewriting $P_\nu(t)$ in the alternative form $P(\nu, t)$, we have, according to Eq. 4,

$$\begin{aligned}P(n, t+\tau)&=P(n+1, t)P_{n+1,n}(\tau)+P(n, t)P_{n,n}(\tau)\\&=k_1(n+1)\tau P(n+1, t)\\&\quad+(1-k_1 n\tau)P(n, t)+o(\tau)\end{aligned}$$

From this we obtain

$$\begin{aligned}\frac{P(n, t+\tau)-P(n, t)}{\tau}&=-k_1 nP(n, t)\\&\quad+k_1(n+1)P(n+1, t)+o(1)\end{aligned}$$

Thus if we let $\tau\to 0$ for fixed t, we have

$$\frac{\mathrm{d}}{\mathrm{d}t}P(n, t)=-k_1 nP(n, t)+k_1(n+1)P(n+1, t) \tag{5}$$

In particular, by assuming $P(n+1, t)=0$ for $n=n_0$, we obtain $\frac{\mathrm{d}}{\mathrm{d}t}P(n_0, t)=-k_1 n_0 P(n_0, t)$ in place of Eq. 5, and for $n=0$, Eq. 5 is reduced to $\frac{\mathrm{d}}{\mathrm{d}t}P(0, t)=k_1 P(1, t)$. Hence Eq. 5 holds for all values of n. Solving Eq. 5 under the conditions (3), we obtain the binomial distribution

$$P(n, t)=\binom{n_0}{n}\{\exp(-k_1 t)\}^n\{1-\exp(-k_1 t)\}^{n_0-n} \tag{6}$$

whose derivation will be shown later. Of course, the equation $\sum_{n=0}^{n_0} P(n, t)=1$ holds certainly.

In order to reduce Eq. 5 to the equation of the mean value for the number of reactant molecules, if we multiply both sides of Eq. 5 by n and summing over all values of n, we get

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\sum_{n=0}^{n_0} nP(n, t)&=-k_1\sum_{n=0}^{n_0} n^2 P(n, t)\\&\quad+k_1\sum_{n=0}^{n_0} n(n-1)P(n, t)\end{aligned}$$

that is,

$$\frac{\mathrm{d}\langle n\rangle}{\mathrm{d}t}=-k_1\langle n\rangle \tag{7}$$

where $\sum_{n=0}^{n_0} nP(n, t)=\langle n\rangle$ denotes the mean value for the number of reactant molecules at time t. This equation is consistent "in the mean" with the deterministic rate equation $\frac{\mathrm{d}n}{\mathrm{d}t}=-k_1 n$, excepting the chance fluctuations* which arise inherently in the reaction itself and are not associated with random experimental errors.

We have so far discussed the stochastic model for such a true unimolecular reaction as the rate constant k_1 is invariable with time, but we can easily extend this to the more general cases in which the rate constants are variable with time. Using in place of k_1 the "instantaneous" value $k(t)$ of the rate constant which is able to take different values at different points on the time axis, we have, instaed of Eq. 5,

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}P(n, t)&=-k(t)nP(n, t)\\&\quad+k(t)(n+1)P(n+1, t)\end{aligned} \tag{8}^{*}$$

In order to solve this equation, we introduce the generating function $\varphi(t, x)=\sum_{n=0}^{n_0} x^n P(n, t)$, which is convergent for $|x|\leq 1$ and defined so that the coefficient of x^n is the probability of finding n reactant molecules at time t in the reaction system. Multiplying both sides of Eq. 8 by x^n and summing from $n=0$ to $n=n_0$, we have

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\sum_{n=0}^{n_0} x^n P(n, t)&=-k(t)\sum_{n=0}^{n_0} nx^n P(n, t)\\&\quad+k(t)\sum_{n=0}^{n_0} nx^{n-1}P(n, t)\end{aligned}$$

Substituting $\frac{\partial\varphi}{\partial t}=\frac{\mathrm{d}}{\mathrm{d}t}\sum_{n=0}^{n_0} x^n P(n, t)$ and $x\frac{\partial\varphi}{\partial x}=\sum_{n=0}^{n_0} nx^n P(n, t)$ into this equation, we obtain the first-order partial differential equation

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* cf. Eq. 22.

** This equation refers to non-stationary process with $k(t)$ depending on time. Since, however, Eq. 5 has the purely "localized" property, the method by which we have derived Eq. (5) is completely applicable to such Markov processes as are not temporally homogeneous.

$$\frac{\partial \varphi}{\partial t}=k(t)(1-x)\frac{\partial \varphi}{\partial x} \qquad (9)$$

The auxiliary differential equation of Eq. 9 is given by

$$\frac{dx}{k(t)(1-x)}=\frac{\mathrm{d}t}{-1}$$

Solving this, we obtain

$$(1-x)\exp\left(-\int_0^t k(t)\mathrm{d}t\right)=\text{constant}$$

According to the theory of partial differential equation the general solution of Eq. 9 is then given by

$$\varphi(t,x)=f\left((1-x)\exp\left(-\int_0^t k(t)\mathrm{d}t\right)\right) \qquad (10)$$

where f is an arbitrary function which is to be determined by the initial condition; the function f is led to the form $f(1-x)=x^{n_0}$ by $\varphi(0,x)=f(1-x)$ and $\varphi(0,x)=\sum_{n=0}^{n_0}x^nP(n,0)=x^{n_0}$, where the initial condition (3) has been used. If we replace $1-x$ by ξ, we obtain the relation $f(\xi)=(1-\xi)^{n_0}$. Again, replacing ξ by $(1-x)\exp\left(-\int_0^t k(t)\mathrm{d}t\right)$, we can transform Eq. 10 into the form

$$\varphi(t,x)=\left\{\left(1-\exp\left(-\int_0^t k(t)\mathrm{d}t\right)\right)+x\exp\left(-\int_0^t k(t)\mathrm{d}t\right)\right\}^{n_0} \qquad (11)$$

which satisfies the condition $\varphi(t,1)=1$, i.e., $\sum_{n=0}^{n_0}P(n,t)=1$. Hence expanding the r. h. s. of Eq. (11), we obtain the binomial distribution by the definition of the generating function,

$$P(n,t)=\binom{n_0}{n}\left(\exp\left(-\int_0^t k(t)\mathrm{d}t\right)\right)^n \times\left(1-\exp\left(-\int_0^t k(t)\mathrm{d}t\right)\right)^{n_0-n} \qquad (12)$$

Since the mean value for the number of reactant molecules at time t is given by $\langle n\rangle=\left(x\frac{\partial\varphi}{\partial x}\right)_{x=1}$, we can easily find

$$\langle n\rangle=n_0\exp\left(-\int_0^t k(t)\mathrm{d}t\right) \qquad (13)$$

If $k(t)$ is set equal to k_1 invariable with time, the above equation becomes $\langle n\rangle=n_0\exp(-k_1t)$, which agrees with the integral of Eq. 7. Such stochastic processes with the variable parameter $k(t)$ can be applied to such various cases as will be described below.

Example 1. Bimolecular Reaction. — The deterministic rate of the bimolecular reaction $2A\rightarrow A_2$ is expressed in the form

$$\frac{\mathrm{d}(2n)}{\mathrm{d}t}=-k_2(2n)^2 \qquad (1,1)$$

where $2n$ denotes the number of reactant molecules at time t and k_2 the rate constant. Solving Eq. 1, 1 under the initial condition that $2n=2n_0$ at $t=0$, we obtain

$$2n=\frac{2n_0}{1+k_2(2n_0)t} \qquad (1,2)$$

or if we set $2n=N$, this becomes

$$N=\frac{N_0}{1+k_2N_0t} \qquad (1,3)$$

From Eq. 1, 2 the probability that any one of n reactant molecules undergoes a chemical transformation during the time interval $(t, t+\Delta t)$ is given by

$$\frac{|\Delta n|}{n}=\frac{k_2N_0}{1+k_2N_0t}\Delta t+o(\Delta t) \qquad (1,4)$$

If we set $\frac{k_2N_0}{1+k_2N_0t}=k(t)$, then we have according to Eq. 8

$$\frac{\mathrm{d}}{\mathrm{d}t}P(n,t)=-\frac{k_2N_0}{1+k_2N_0t}nP(n,t)+\frac{k_2N_0}{1+k_2N_0t}(n+1)P(n+1,t) \qquad (1,5)$$

Multiplying both sides of Eq. 1, 5 by n and summing over all values of n, we obtain as the differential equation concerning the mean value for the number of reactant molecules

$$\frac{\mathrm{d}\langle n\rangle}{\mathrm{d}t}=-\frac{k_2N_0}{1+k_2N_0t}\langle n\rangle \qquad (1,6)$$

or

$$\frac{\mathrm{d}\langle N\rangle}{\mathrm{d}t}=-\frac{k_2N_0}{1+k_2N_0t}\langle N\rangle \qquad (1,7)$$

whose solution is given by

$$\langle N\rangle=\frac{N_0}{1+k_2N_0t} \qquad (1,8)$$ [*]

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[*] In general we have as the stochastic model for the bimolecular reaction $2A\rightarrow A_2$

$$\frac{\mathrm{d}}{\mathrm{d}t}P(2n,t)=-k_2\frac{(2n)(2n-1)}{2}P(2n,t)+k_2\frac{\{2(n+1)\}\{2n+1)-1\}}{2}P(2(n+1),\mathrm{t}) \qquad (1)$$

Transforming this into the differential equation of the mean value, we obtain

$$\frac{\mathrm{d}\langle 2n\rangle}{\mathrm{d}t}=-k_2(\langle(2n)^2\rangle-\langle 2n\rangle) \qquad (2)$$

If we set $2n=N$, we have in place of Eq. 2

$$\frac{\mathrm{d}\langle N\rangle}{\mathrm{d}t}=-k_2(\langle N^2\rangle-\langle N\rangle) \qquad (2)'$$

Solving this under the initial condition that $N=N_0$ at $t=0$, we obtain

$$\langle N\rangle=\frac{N_0}{1+k_1N_0t+k_2N_0\int_0^t\frac{\sigma^2(t)-\langle N\rangle}{\langle N\rangle^2}\mathrm{d}t} \qquad (3)$$

where N_0 is the initial number of reactant molecules and $\sigma^2(t)=\langle N^2\rangle-\langle N^2\rangle$ denotes the variance.

for the initial condition that $N=N_0$ at $t=0$. It should be here noted that Eq. 1, 8 agrees "in the mean" with the result derived by the deterministic theory. If we multiply both sides of Eq. 1, 5 by n^2 and sum over all values of n, we obtain as the differential equation for the second moment $\langle n^2\rangle$

$$\frac{\mathrm{d}\langle n^2\rangle}{\mathrm{d}t}=-2\frac{k_2N_0}{1+k_2N_0t}\langle n^2\rangle+\frac{k_2N_0}{1+k_2N_0t}\langle n\rangle \tag{1, 9}$$

which is transformed into the form, according to $2n=N$ and Eq. 1, 8,

$$\frac{\mathrm{d}\langle N^2\rangle}{\mathrm{d}t}+2\frac{k_2N_0}{1+k_2N_0t}\langle N^2\rangle=2k_2\left(\frac{N_0}{1+k_2N_0t}\right)^2 \tag{1, 10}$$

Solving Eq. 1, 10 under the initial condition that $N=N_0$ at $t=0$, we obtain

$$\langle N^2\rangle=\left(\frac{N_0}{1+k_2N_0t}\right)^2+2k_2t\left(\frac{N_0}{1+k_2N_0t}\right)^2 \tag{1, 11}$$

Substituting Eq. 1, 8 into this equation, we have as the variance $\sigma^2(t)=\langle N^2\rangle-\langle N\rangle^2$

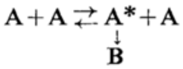
$$\sigma^2(t)=2k_2t\langle N\rangle^2 \tag{1, 12}$$

and consequently the coefficient of variation $\delta(t)=\dfrac{\sigma(t)}{\langle N\rangle}$ is expressed in the form

$$\delta(t)=\sqrt{2k_2t} \tag{1, 13}$$

For sufficiently large values of t, the coefficient of variation, which is independent of the initial number of reactant molecules, is considerably large, so that the statistical fluctuation arising inherently in the bimolecular reaction itself may become large compared with the random experimental errors incidental to the observed value $\langle N\rangle$.

Example 2. Lindemann's Mechanism. — Let us consider the collision theory for the unimolecular reaction which is usually associated with the name of Lindemann[10].



$$\begin{array}{c}\mathrm{A+A}\rightleftarrows\mathrm{A^*+A}\\ \quad\;\downarrow\\ \quad\;\mathrm{B}\end{array}$$

The reaction $\mathrm{A+A\rightarrow A^*+A}$ is the activation process by the collision between two inert reactant molecules, the reverse reaction $\mathrm{A+A^*\rightarrow A+A}$ is the deactivation process by the collision between an inert reactant molecule and an activated molecule and the spontaneous reaction $\mathrm{A^*\rightarrow B}$ is the "true" unimolecular reaction. If we denote by $P(n_\mathrm{a}, n_\mathrm{a}^*, n_\mathrm{b}, t)$ the probability that n_a inert reactant molecules, n_a^* activated molecules and n_b resultant molecules coexist in the reaction system at time t, then we have

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}&P(n_\mathrm{a}, n_\mathrm{a}^*, n_\mathrm{b}, t)\\ &=-k^*(t)n_\mathrm{a}P(n_\mathrm{a}, n_\mathrm{a}^*, n_\mathrm{b}, t)\\ &\quad+k^*(t)(n_\mathrm{a}+1)P(n_\mathrm{a}+1, n_\mathrm{a}^*-1, n_\mathrm{b}, t)\\ &\quad-k'(t)n_\mathrm{a}^*P(n_\mathrm{a}, n_\mathrm{a}^*, n_\mathrm{b}, t)\\ &\quad+k'(t)(n_\mathrm{a}^*+1)P(n_\mathrm{a}-1, n_\mathrm{a}^*+1, n_\mathrm{b}, t)\\ &\quad-kn_\mathrm{a}^*P(n_\mathrm{a}, n_\mathrm{a}^*, n_\mathrm{b}, t)\\ &\quad+k(n_\mathrm{a}^*+1)P(n_\mathrm{a}, n_\mathrm{a}^*+1, n_\mathrm{b}-1, t)\end{aligned} \tag{2, 1}$$

where $k^*(t)$ and $k'(t)$ denote the instantaneous values of the rate constants for the reactions $\mathrm{A+A\rightarrow A^*+A}$ and $\mathrm{A+A^*\rightarrow A+A}$ respectively and k the rate constant for the true unimolecular reaction $\mathrm{A^*\rightarrow B}$. Thus the differential equations for the mean values $\langle n_\mathrm{a}\rangle$ and $\langle n_\mathrm{a}^*\rangle$ are given by

$$\frac{\mathrm{d}\langle n_\mathrm{a}\rangle}{\mathrm{d}t}=-k^*(t)\langle n_\mathrm{a}\rangle+k'(t)\langle n_\mathrm{a}^*\rangle \tag{2, 2}$$

and

$$\frac{\mathrm{d}\langle n_\mathrm{a}^*\rangle}{\mathrm{d}t}=k^*(t)\langle n_\mathrm{a}\rangle-(k'(t)+k)\langle n_\mathrm{a}^*\rangle \tag{2, 3}$$

respectively, which are consistent "in the mean" with Fowler's equations[11].

Multitdimensional Stochastic Model

In comparing the probabilistic theory with the deterministic theory, we have so far considered the one-dimensional stochastic process for the "true" unimolecular gas reaction on the macroscopic point of view. Now consider microscopically the multi-dimensional stochastic process for a reaction system, such that at time t the numbers of reactant molecules in the states of internal energies $\varepsilon_1, \varepsilon_2, \cdots\cdots, \varepsilon_i, \cdots\cdots$ are $n_1, n_2, \cdots\cdots, n_i, \cdots\cdots$, respectively, under the same conditions as in the previous section. Then if we denote the probability for this reaction system by $P(n_1, n_2, \cdots\cdots, n_i, \cdots\cdots, t)=P(\{n_i\}, t)$, we have

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[10] F. A. Lindemann, *Trans. Faraday. Soc.*, 17, 599 (1921).

[11] R. H. Fowler, "Statistical Mechanics", Cambridge University Press (1936), p. 712.

* The internal energy ε_i of reactant molecule changes continually into the enregy ε with various values by the random energy transfer between molecules. Expressing the distribution of such energy ε by $F_i(\varepsilon)$, we have as the averaged specific reaction rate $\langle k_1(\varepsilon_i)\rangle$

$$\langle k_1(\varepsilon_i)\rangle=\int_0^\infty k_1(\varepsilon/\varepsilon_i)\mathrm{d}F_i(\varepsilon),$$

where we may take such distribution function that $F_i(0)=0$ and $F_i(\infty)=1$, and $k_1(\varepsilon/\varepsilon_i)=0$ if ε is smaller then the value necessary for a chemical reaction to occur. The $k_1^{(i)}$ in Eq. 14 denotes such $\langle k_1(\varepsilon_i)\rangle$.

$$
\begin{aligned}
&\frac{\mathrm{d}}{\mathrm{d}t}P(n_1, n_2, \cdots\cdots, n_i, \cdots\cdots, t)\\
&= -k_1{}^{(1)}n_1P(n_1, n_2, \cdots\cdots, n_i, \cdots\cdots, t)\\
&\quad +k_1{}^{(1)}(n_1+1)P(n_1+1, n_2, \cdots\cdots, n_i, \cdots\cdots, t)\\
&\quad -k_1{}^{(2)}n_2P(n_1, n_2, \cdots\cdots, n_i, \cdots\cdots, t)\\
&\quad +k_1{}^{(2)}(n_2+1)P(n_1, n_2+1, \cdots\cdots, n_i, \cdots\cdots, t)\\
&\quad \vdots\\
&\quad -k_1{}^{(i)}n_iP(n_1, n_2, \cdots\cdots, n_i, \cdots\cdots, t)\\
&\quad +k_1{}^{(i)}(n_i+1)P(n_1, n_2, \cdots\cdots, n_i+1, \cdots\cdots, t)\\
&\quad \vdots
\end{aligned}
\tag{14}
$$

or

$$
\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}P(\{n_i\}, t) &= -\sum_i k_1{}^{(i)}n_iP(\{n_j\}_{j\neq i}, n_i, t)\\
&\quad +\sum_i k_1{}^{(i)}(n_i+1)P(\{n_j\}_{j\neq i}, n_i+1, t)
\end{aligned}
\tag{14$'$}
$$

where $P(\{n_j\}_{j\neq i}, n_i+1, t)=P(n_1, n_2, \cdots\cdots, n_{i-1}, n_i+1, n_{i+1}, \cdots\cdots, t)$ and the rate constant $k_1{}^{(i)*}$ which is the function of energy ε_i denotes the transition probability that a molecule in the internal state with an energy ε_i is transformed into a resultant molecule during unit time. Let the total number of reactant molecules at time t be $n=\sum_i n_i$ and the initial number of reactant molecules with the internal energy ε_i be $n_i{}^0$. If we multiply both sides of Eq. 14 by $\sum n_i$ and sum from 0 to $n_i{}^0$ $(i=1, 2, \cdots\cdots)$ with respect to each energy state, we obtain

$$
\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}\langle\sum_i n_i\rangle &= -\langle k_1{}^{(1)}n_1\sum_i n_i\rangle+\langle k_1{}^{(1)}n_1(\sum_i n_i-1)\rangle\\
&\quad -\langle k_1{}^{(2)}n_2\sum_i n_i\rangle+\langle k_1{}^{(2)}n_2(\sum_i n_i-1)\rangle\\
&\qquad \vdots\\
&\quad -\langle k_1{}^{(i)}n_i\sum_i n_i\rangle+\langle k_1{}^{(i)}n_i(\sum_i n_i-1)\rangle\\
&\qquad \vdots\\
&= -\langle\sum_i k_1{}^{(i)}n_i\rangle
\end{aligned}
$$

that is,

$$
\frac{\mathrm{d}\langle n\rangle}{\mathrm{d}t} = -\langle\sum_i k_1{}^{(i)}n_i\rangle \tag{15}
$$

Here if we set

$$
\frac{\sum_i k_1{}^{(i)}n_i}{\sum_i n_i} = \overline{k}_1 \tag{16}
$$

Eq. 15 becomes, according to $\sum_i k_1{}^{(i)}n_i=\overline{k}_1 n$,

$$
\frac{\mathrm{d}\langle n\rangle}{\mathrm{d}t} = -\overline{k}_1\langle n\rangle \tag{17}
$$

which formally agrees with Eq. 7. The rate constant $\overline{k}_1$ denotes the "average" probability that one molecule undergoes a chemical transformation during unit time. On comparing Eq. 17 with the conventional rate equation

$$
\frac{\mathrm{d}n}{\mathrm{d}t} = -\overline{k}_1 n, \tag{18}
$$

which is statistical only with respect to the rate constant but deterministic with respect to the number of reactant molecules, it should be noticed that the application of the multi-dimensional stochastic model to the "true" unimolecular gas reaction presents us with an excellent method for calculating statistically the rate constant together with the number of reactant molecules.

In order to calculate the variance of the total number of reactant molecules, if we multiply both sides of Eq. 14′ by $(\sum_i n_i)^2$ and sum over all values of each n_i we obtain as the differential equation of the mean value for $(\sum_i n_i)^2$

$$
\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}\langle(\sum_i n_i)^2\rangle &= -2\langle(\sum_i k_1{}^{(i)}n_i)(\sum_i n_i)\rangle\\
&\quad +\langle\sum_i k_1{}^{(i)}n_i\rangle
\end{aligned}
$$

Using $\sum_i n_i=n$ and $\sum_i k_1{}^{(i)}n_i=\overline{k}_1 n$, we can transform this to

$$
\frac{\mathrm{d}\langle n^2\rangle}{\mathrm{d}t} = -2\overline{k}_1\langle n^2\rangle+\overline{k}_1\langle n\rangle \tag{19}
$$

When we rewrite Eq. 17 by the alternative equation

$$
\frac{\mathrm{d}\langle n\rangle^2}{\mathrm{d}t} = -2\overline{k}_1\langle n\rangle^2 \tag{20}
$$

and subtract Eq. 20 from Eq. 19, we obtain, using $(n)=n_0\exp(-\overline{k}_1 t)$,

$$
\begin{aligned}
&\frac{\mathrm{d}}{\mathrm{d}t}(\langle n^2\rangle-\langle n\rangle^2)+2\overline{k}_1(\langle n^2\rangle-\langle n\rangle^2)\\
&\qquad =\overline{k}_1 n_0\exp(-\overline{k}_1 t)
\end{aligned}
\tag{21}
$$

Solving Eq. 21 with respect to the variance $\langle n^2\rangle-\langle n\rangle^2$, we obtain

$$
\langle n^2\rangle-\langle n^2\rangle=n_0\exp(-\overline{k}_1 t)\{1-\exp(-\overline{k}_1 t)\} \tag{22}
$$

which agrees with the variance in Bartholomay's macroscopic treatment if we use k_1 in place of $\overline{k}_1$. We observe, however, that $\overline{k}_1$ is estimated by the method to be shown below.

In the reaction system at thermal equilibrium the equilibrium fraction of reactant molecules in the energy state ε_i is given by

$$
n_i=n\frac{g(\varepsilon_i)\exp(-\varepsilon_i/\boldsymbol{k}T)}{\sum_i g(\varepsilon_i)\exp(-\varepsilon_i/\boldsymbol{k}T)} \tag{23}
$$

where $g(\varepsilon_i)$ denotes the quantum statistical weight for the state of energy ε_i. Substituting Eq. 23 into Eq. 16, we find

$$\bar{k}_1=\frac{\sum\limits_i k_1^{(i)}(\varepsilon_i)g(\varepsilon_i)\exp(-\varepsilon_i/\boldsymbol{k}T)}{\sum\limits_i g(\varepsilon_i)\exp(-\varepsilon_i/\boldsymbol{k}T)} \tag{24}$$

If we differentiate logarithmically with respect to T, we obtain

$$kT^2\frac{\partial\ln\bar{k_1}}{\partial T}=\frac{\sum\limits_i\varepsilon_i k_1^{(i)}(\varepsilon_i)g(\varepsilon_i)\exp(-\varepsilon_i/\boldsymbol{k}T)}{\sum\limits_i k_1^{(i)}(\varepsilon_i)g(\varepsilon_i)\exp(-\varepsilon_i/\boldsymbol{k}T)}$$

$$-\frac{\sum\limits_i\varepsilon_i g(\varepsilon_i)\exp(-\varepsilon_i/\boldsymbol{k}T)}{\sum\limits_i g(\varepsilon_i)\exp(-\varepsilon_i/\boldsymbol{k}T)} \tag{25}$$

where the first term on the r. h. s. is the average internal energy, not of the existing energized molecules, but of those which react during unit time and the second term is the average internal energy for all molecules[12]. If all reacting molecules that possess energy exceeding ε_0 have the same probability λ_0 for the "true" unimolecular reaction during unit time, then we have the following relations;

$$k_1^{(i)}=0 \quad \text{for} \quad \varepsilon_i<\varepsilon_0,$$
$$k_1^{(i)}=\lambda_0 \quad \text{for} \quad \varepsilon_i\gtrsim\varepsilon_0.$$

Eq. 24 is therefore transformed into

$$\bar{k}_1=\frac{\lambda_0\sum\limits_{\varepsilon_i\geq\varepsilon_0}g(\varepsilon_i)\exp(\varepsilon_i/\boldsymbol{k}T)}{\sum\limits_i g(\varepsilon_i)\exp(-\varepsilon_i/\boldsymbol{k}T)} \tag{26}$$

If we treat the internal vibration of molecule as consisting of linear harmonic oscillators whose energy levels are continuous, we have $g(\varepsilon)\propto\varepsilon^{s-1}\varDelta\varepsilon$ within a certain range of $\varDelta\varepsilon$ and can approximate the r. h. s. of Eq. 26 by the distribution function of $\varGamma$-type

$$\frac{\lambda_0}{\varGamma(s)}\int_{\varepsilon_0}^{\infty}\left(\frac{\varepsilon}{\boldsymbol{k}T}\right)^{s-1}\exp(-\varepsilon/kT)\frac{\mathrm{d}\varepsilon}{\boldsymbol{k}T}$$

where $\varGamma(s)=(s-1)!$. Hence we have in place of Eq. 26

$$\bar{k}_1\simeq\lambda_0\exp(-\xi_0/\boldsymbol{k}T)\sum_{r=0}^{s-1}\frac{1}{r!}\left(\frac{\varepsilon_0}{\boldsymbol{k}T}\right)^r \tag{27}$$

where ε_0 denotes the minimum energy required for reaction. But if $\varepsilon_0\gg s\boldsymbol{k}T$, the overall rate constant $\bar{k}_1$ is approximately given by

$$\bar{k}_1\simeq\frac{\lambda_0}{\varGamma(s)}\left(\frac{\varepsilon_0}{\boldsymbol{k}T}\right)^{s-1}\exp(-\varepsilon_0/\boldsymbol{k}T) \tag*{(27)$'$}$$

And more generally, if we denote the probability for the distribution of higher energy levels than ε_0 by $g(\varepsilon_i-\varepsilon_0)/g(\varepsilon_i)$, $k_1^{(i)}$, the specific reaction rate for molecules of energy $\varepsilon_i\gtrsim\varepsilon_0$, is proportional to this probability. We then have the relations

$$k_1^{(i)}=0 \quad \text{for} \quad \varepsilon_i<\varepsilon_0$$
$$k_1^{(i)}=Ag(\varepsilon_i-\varepsilon_0)/g(\varepsilon_i) \quad \text{for} \quad \varepsilon_i\gtrsim\varepsilon \tag{28}$$

where A is the proportional coefficient and we define $g(\varepsilon_i-\varepsilon_0)=0$ for $\varepsilon_i\leq\varepsilon_0$. Thus substituting Eq. 28 into Eq. 24, we obtain

$$\bar{k}_1=A\exp(-\varepsilon_0/\boldsymbol{k}T)$$
$$\times\frac{\sum\limits_{\varepsilon_i\geq\varepsilon_0}g(\varepsilon_i-\varepsilon_0)\exp\{-(\varepsilon_i-\varepsilon_0)\boldsymbol{k}T\}}{\sum\limits_i g(\varepsilon_i)\exp(-\varepsilon_i/\boldsymbol{k}T)}$$
$$=A\exp(-\varepsilon_0/\boldsymbol{k}T)\frac{\sum\limits_{\varepsilon_i'}g(\varepsilon_i')\exp(-\varepsilon_i'/\boldsymbol{k}T)}{\sum\limits_i g(\varepsilon_i)\exp(-\varepsilon_i/\boldsymbol{k}T)}$$

where $\varepsilon_i'=\varepsilon_i-\varepsilon_0$. If, however, we use the same model molecule composed of a set of simple harmonic oscillators of equal frequency as in Kassel's theory[13], $\sum\limits_{\varepsilon_i'}g(\varepsilon_i')\exp(-\varepsilon_i'/\boldsymbol{k}T)$ is equal to $\sum\limits_i g(\varepsilon_i)\exp(-\varepsilon_i/\boldsymbol{k}T)$, and consequently we obtain the Arrhenius' equation

$$\bar{k}_1=A\exp(-\varepsilon_0/\boldsymbol{k}T) \tag{29}$$

And from Eqs. 28 and 29 $k_1^{(i)}$ is given by

$$k_1^{(i)}=\bar{k}_1\exp(-\varepsilon_0/\boldsymbol{k}T)\frac{g(\varepsilon_i-\varepsilon_0)}{g(\varepsilon_i)} \tag{30}$$

where $\varepsilon_i\gtrsim\varepsilon_0$.

Conclusions

We have clarified the probabilistic foundations for the application of the theory of the stochastic process to the " true " unimolecular reaction. By extending Bartholomay's method to the more general stochastic process having the parameter $k(t)$ variable with time, we have shown that the theory of stochastic process can be applied to any chemical reaction other than the unimolecular reaction. We have also noticed that the averaged rate constant $\bar{k_1}$ of the "true" unimolecular reaction is legitimately calculated by the application of the multidimensional stochastic process to the chemical reaction.

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