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Stochastic Model for Chemical Relaxation

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The stochastic formulation of chemical rate equations requires that the process of chemical relaxation should be accompanied with the fluctuation of chemical composition. It is shown that the factor Γ, which Eigen and de Maeyer introduced in the thermodynamic analyses of chemical relaxations, may be interpreted as the fluctuation of chemical composition.

For chemical phenomena, in general, the concept of fluctuation is almost out of question. According to the stochastic theory of chemical kinetics,[1] the fluctuation of chemical composition in an ordinary reaction system is negligibly small compared with the mean value derived from the deterministic theory.[2] There is, however, a chemical phenomenon for which the fluctuation of chemical composition may become an important factor to the description of chemical rate process. It is chemical relaxation. The chemical relaxation we treat in this paper is the process of equilibriation to a constant stationary state after a stepwise perturbation due to the change of a state variable (*e.g.*, temperature jump). If such a chemical relaxation is stochastically treated the fluctuation of chemical composition is explicitly included in the integrated relaxation equation through the relation to equilibrium constant. It is of significance that the stochastic theory of chemical kinetics makes it possible to relate the fluctuation of chemical composition to equilibrium constant.

One-step Reaction

As an introduction to the stochastic model for

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[1] For an extensive review of this work, see D. A McQuarrie, "Stochastic Approach to Chemical Kinetics," Methuen, London (1967).

[2] It has been recently discussed by Oppenheim *et al.* that the stochastic formulation must be reduced to the deterministic formulation in the thermodynamic limit: $N\to\infty$, $V\to\infty$, N/V is constant, where N is the total number of molecules in the system with volume V (I. Oppenheim, K. E. Shuler and G. H. Weiss, *J. Chem. Phys.*, **50**, 460 (1969)).

chemical relaxation, we consider the case of one-step reaction $A \rightleftharpoons B$ taking place in a closed system.

Let $P_{n_A,n_B}(t)$ be the probability that the number of A and B molecules found in the reacting system at time t are n_A and n_B, respectively. According to the stochastic theory of chemical kinetics, then, it follows that the probability distribution $P_{n_A^{(0)},n_B^{(0)}}(0)$ for the system in the initial chemical equilibrium is given by

$$P_{n_A^{(0)},n_B^{(0)}}(0) = \frac{N!}{n_A^{(0)}!\,n_B^{(0)}!}\left(\frac{k_{-1}^{(0)}}{k_1^{(0)}+k_{-1}^{(0)}}\right)^{n_A^{(0)}} \times\left(\frac{k_1^{(0)}}{k_1^{(0)}+k_{-1}^{(0)}}\right)^{n_B^{(0)}} \tag{1}$$

where $N=n_A^{(0)}+n_B^{(0)}$ is the total number of molecules in the system and $k_1^{(0)}$ and $k_{-1}^{(0)}$ denote the transition probabilities per one molecule and per unit time for the reactions A→B and B→A, respectively.[3] If the system governed by the equilibrium probability distribution (1) is disturbed by changing one of the external state variables, which define the thermodynamic equilibrium for the system, it approaches its new stable equilibrium in the manner described by the equation

$$\begin{aligned} \mathrm{d}P_{n_A,n_B}(t)/\mathrm{d}t = {}& k_1(n_A+1)P_{n_A+1,n_B-1}(t) \\ & -(k_1 n_A + k_{-1}n_B)P_{n_A,n_B}(t) \\ & +k_{-1}(n_B+1)P_{n_A-1,n_B+1}(t) \\ & (0 \leqq n_A, n_B \leqq N) \end{aligned} \tag{2}$$

on the basis of the idea that chemical reaction is Markov process homogeneous in time. In this equation, k_1 and k_{-1} are the transition probabilities in the relaxing system and $P_{N+1,-1}(t)=P_{-1,N+1}(t)=0$ is assumed. Solving Eq. (2) under the initial condition (1), we obtain the binomial distribution

$$P_{n_A,n_B}(t) = \frac{N!}{n_A!\,n_B!}\{p_A(t)\}^{n_A}\{p_B(t)\}^{n_B} \tag{3}$$

where

$$p_A(t) = \frac{k_{-1}}{k_1+k_{-1}} + \frac{\dfrac{k_{-1}^{(0)}}{k_1^{(0)}+k_{-1}^{(0)}}k_1 - \dfrac{k_1^{(0)}}{k_1^{(0)}+k_{-1}^{(0)}}k_{-1}}{k_1+k_{-1}}\,\mathrm{e}^{-(k_1+k_{-1})t}$$

and

$$p_B(t) = 1 - p_A(t)$$

Equation (3) represents the probability distribution in the course of the relaxation process under consideration. The expected value of the number of A molecules, $\langle n_A\rangle$, is given by $\langle n_A\rangle = Np_A(t)$. Since the expected value $\langle n_A^{(0)}\rangle$ in the initial equilibrium state is $\langle n_A^{(0)}\rangle = Np_A(0) = Nk_{-1}^{(0)}/(k_1^{(0)}+k_{-1}^{(0)})$, the change of the number of A molecules due to the perturbation, $\Delta\langle n_A\rangle = \langle n_A^{(0)}\rangle - \langle n_A\rangle$, can be written as

$$\Delta\langle n_A\rangle = N\left(\frac{k_{-1}^{(0)}}{k_1^{(0)}+k_{-1}^{(0)}} - \frac{k_{-1}}{k_1+k_{-1}}\right)(1-\mathrm{e}^{-(k_1+k_{-1})t}) \tag{4}$$

or

$$\Delta\langle n_A\rangle = N\left(\frac{1}{K_1^{(0)}+1} - \frac{1}{K_1+1}\right)(1-\mathrm{e}^{-t/\tau_1}) \tag{5}$$

where we have introduced the equilibrium constant $K_1^{(0)}=k_1^{(0)}/k_{-1}^{(0)}$ and $K_1=k_1/k_{-1}$ and the relaxation time $\tau_1=(k_1+k_{-1})^{-1}$.

When the change δZ of an external state variable Z is applied to the system in the initial chemical equilibrium, the equilibrium constant for the relaxing system can be expressed by

$$K_1 = K_1^{(0)}\{1+(\partial \ln K_1/\partial Z)_0 \delta Z\} \tag{6}$$

where the subscript 0 denotes the initial state. Substituting Eq. (6) into Eq. (5), we obtain

$$\Delta\langle n_A\rangle = N\frac{K_1^{(0)}}{(K_1^{(0)}+1)^2}\left(\frac{\partial \ln K_1}{\partial Z}\right)_0 \delta Z(1-\mathrm{e}^{-t/\tau_1}) \tag{7}$$

The initial probability distribution (1), however, has the variance

$$\begin{aligned} \sigma^2(0) &= \langle (n_A^{(0)} - \langle n_A^{(0)}\rangle)^2\rangle \\ &= Nk_1^{(0)}k_{-1}^{(0)}/(k_1^{(0)}+k_{-1}^{(0)})^2 \end{aligned} \tag{8}$$

We now give an elementary discussion of this equation. The factor $k_1^{(0)}/(k_1^{(0)}+k_{-1}^{(0)})$ represents the transition probability per one molecule and per unit time for A→B under the condition that either forward or reverse reaction occurs and similarly the factor $k_{-1}^{(0)}/(k_1^{(0)}+k_{-1}^{(0)})$ the conditional transition probability for B→A. Since, however, the forward and reverse reactions in the reacting system in chemical equilibrium are considered to occur almost

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[3] If Eq. (2) for the reacting system before perturbation is solved with the initial condition $P_{N,0}(0)=1$, Eq. (1) is obtained as the equilibrium probability distribution which is independent of the initial condition.

This probability distribution can be also derived by the statistical-mechanical procedure as follows. In the ideal gas phase reaction, the equilibrium probability distribution for each component is given by the Poisson distribution

$$p(n_\gamma^{(0)}) = \mathrm{e}^{-\lambda_\gamma (p.f.)_\gamma}\{\lambda_\gamma (p.f.)_\gamma\}^{n_\gamma^{(0)}}/n_\gamma^{(0)}! \quad (\gamma = A, B)$$

where λ_γ is the absolute activity of γ-component and $(p.f.)_\gamma$ the partition function. However, as the convolution of Poisson distributions is also the Poisson distribution, the probability distribution for the total number of molecules, $n_A^{(0)}+n_B^{(0)}=N$, is

$$p(N) = \mathrm{e}^{-\{\lambda_A (p.f.)_A + \lambda_B (p.f.)_B\}} \times \{\lambda_A (p.f.)_A + \lambda_B (p.f.)_B\}^N/N!$$

It follows that the conditional probability distribution for an arbitrarily fixed N, $p(n_A^{(0)}, n_B^{(0)}\,|\,N)$, is given by the binomial distribution,

$$\begin{aligned} p(n_A^{(0)}, n_B^{(0)}\,|\,N) &= p(n_A^{(0)})p(n_B^{(0)})/p(N) \\ &= \frac{N!}{n_A^{(0)}!\,n_B^{(0)}!}\left\{\frac{(p.f.)_A}{(p.f.)_A+(p.f.)_B}\right\}^{n_A^{(0)}} \times \left\{\frac{(p.f.)_B}{(p.f.)_A+(p.f.)_B}\right\}^{n_B^{(0)}} \end{aligned}$$

where the thermodynamic condition of chemical equilibrium, $\lambda_A=\lambda_B$, is used. This is equivalent to Eq. (1) because of $(p.f.)_B/(p.f.)_A = \langle n_B^{(0)}\rangle/\langle n_A^{(0)}\rangle = k_1^{(0)}/k_{-1}^{(0)} = K_1^{(0)}$.

simultaneously with various reaction probabilities, the chemical compositions must be more or less fluctuating about the expected values. The fluctuation $\sigma^2(0)$ may therefore be regarded as the expected value of such an event. We then have in place of Eq. (8)

$$\sigma^2(0) = NK_1^{(0)}/(K_1^{(0)} + 1)^2 \tag{9}$$

which tells us the relation of fluctuation to equilibrium constant. On applying Eq. (9) to Eq. (7), we find that

$$\Delta\langle n_A\rangle = \sigma^2(0)\left(\frac{\partial \ln K_1}{\partial Z}\right)_0 \delta Z(1 - e^{-t/\tau_1}) \tag{10}$$

To the same approximation, this can be also written as

$$\Delta\langle n_A\rangle = \sigma^2(\infty)\left(\frac{\partial \ln K_1}{\partial Z}\right)_0 \delta Z(1 - e^{-t/\tau_1}) \tag{11}$$

because the relation between $\sigma^2(0)$ and the fluctuation $\sigma^2(\infty)$ in the new chemical equilibrium is given by

$$\begin{aligned}\sigma^2(\infty) &= NK_1/(K_1 + 1)^2 \\ &\simeq \sigma^2(0)\left\{1 - \frac{K_1^{(0)} - 1}{K_1^{(0)} + 1}\left(\frac{\partial \ln K_1}{\partial Z}\right)_0 \delta Z\right\}\end{aligned} \tag{12}$$

where Eqs. (6) and (9) have been used and $|(K_1^{(0)} - 1)/(K_1^{(0)} + 1)| < 1$ holds for all possible values of $K_1^{(0)}$.

It is instructive to compare such a stochastic analysis with the theory of Eigen and de Maeyer. We transform the fluctuation $\sigma^2(\infty)$ as follows:

$$\begin{aligned}\sigma^2(\infty) &= Np_A(\infty)\{1 - p_A(\infty)\} \\ &= \langle n_A\rangle_\infty \langle n_B\rangle_\infty / N \\ &= (1/\langle n_A\rangle_\infty + 1/\langle n_B\rangle_\infty)^{-1}\end{aligned} \tag{13}$$

where $\langle n_A\rangle_\infty = Np_A(\infty)$ and $\langle n_B\rangle_\infty = Np_B(\infty)$ are the mean numbers of A and B molecules in the new chemical equilibrium, respectively. The last expression of Eq. (12) is in form in agreement with the factor Γ that Eigen and de Maeyer have introduced through the thermodynamic considerations of chemical relaxations.[4]

According to the stochastic nonequilibrium thermodynamics of chemical reactions,[5] the fluctuation $\sigma^2(\infty)$ can be closely correlated to the chemical affinity A by

$$\sigma^2(\infty) = \left\{-\frac{1}{\boldsymbol{k}T}\left(\frac{\partial A}{\partial \xi}\right)_\infty\right\}^{-1} \tag{14}$$

where $\boldsymbol{k}$ is Boltzmann's constant, T the temperature of the relaxing system in chemical equilibrium and ξ the degree of advancement. Since the chemical affinity is expressed in the form

$$A = \boldsymbol{k}T\{\ln(\langle n_A\rangle/\langle n_A\rangle_\infty) - \ln(\langle n_B\rangle/\langle n_B\rangle_\infty)\}$$

it can be easily shown that Eq. (14) is equivalent to Eq. (13). From the stochastic point of view, therefore, the factor Γ of Eigen and de Maeyer is to be interpreted as the fluctuation of chemical composition.

To test this theory for other chemical relaxations, we take a second-order reaction $A+B \rightleftarrows C$ as an example. The stochastic process for this reaction is described by

$$\begin{aligned}dP_{n_C}(t)/dt = {} & k_2\{n_A^{(0)} - (n_C - 1 - n_C^{(0)})\} \\ & \times \{n_B^{(0)} - (n_C - 1 - n_C^{(0)})\}P_{n_C-1}(t) \\ & - [k_2\{n_A^{(0)} - (n_C - n_C^{(0)})\} \\ & \times \{n_B^{(0)} - (n_C - n_C^{(0)})\} + k_{-2}n_C]P_{n_C}(t) \\ & + k_{-2}(n_C + 1)P_{n_C+1}(t)\end{aligned} \tag{15}$$

where $P_{n_C}(t)$ denotes the probability that the number of molecules of chemical species C existing in the relaxing system at time t is n_C, $n_A^{(0)}$, $n_B^{(0)}$ $(\geq n_A^{(0)})$ and $n_C^{(0)}$ are the numbers of A, B and C molecules in the initial chemical equilibrium and k_2 and k_{-2} the transition probabilities per molecule and per unit time for the forward and reverse reactions, respectively. Since the difference between $\sigma^2(0)$ and $\sigma^2(\infty)$ is not so large, as is clear from Eq. (12), it has been assumed that the numbers of A, B and C molecules in the initial chemical equilibrium are given by $n_A^{(0)}$, $n_B^{(0)}$ are $n_C^{(0)}$ in the probabilistic mean of $P_{n_A^{(0)}, n_B^{(0)}, n_C^{(0)}}(0) = 1$. If the inequality $n_C - n_C^{(0)} \ll n_A^{(0)}, n_B^{(0)}$, which corresponds to the linear approximation in the usual analysis of chemical relaxation, holds during the relaxation process, Eq. (15) is reduced to

$$\begin{aligned}dP_{n_C}(t)/dt = {} & k_2\{(n_A^{(0)}n_B^{(0)} + n_B^{(0)}n_C^{(0)} + n_C^{(0)}n_A^{(0)}) \\ & - (n_A^{(0)} + n_B^{(0)})(n_C - 1)\}P_{n_C-1}(t) \\ & - [k_2\{(n_A^{(0)}n_B^{(0)} + n_B^{(0)}n_C^{(0)} + n_C^{(0)}n_A^{(0)}) \\ & - (n_A^{(0)} + n_B^{(0)})n_C\} + k_{-2}n_C]P_{n_C}(t) \\ & + k_{-2}(n_C + 1)P_{n_C+1}(t)\end{aligned} \tag{15'}$$

Solving this differential-difference equation by the use of the generating function of $P_{n_C}(t)$,

$$G(\theta, t) = \sum_{n_C=0}^{\infty} \theta^{n_C} P_{n_C}(t), \qquad |\theta| \leqq 1$$

we obtain, as the solution subject to the initial condition

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[4] M. Eigen and L. de Maeyer, "Technique of Organic Chemistry," 2nd Ed., Vol. VIII, part 2, ed. by S. L. Fries, E. S. Lewis and A. Weissberger, Interscience Publishers, Inc., New York, N. Y. (1963), p. 934. In deriving the thermodynamic relation of the change of concentration to that of equilibrium constant, they have defined the factor $\Gamma_m = 1/(\sum_i \nu_i^2/\overline{m}_i)$, where ν_i is the stoichiometric coefficient and $\overline{m}_i$ the molality in chemical equilibrium state. The index of Γ, however, changes with the kind of concentration variable. Whatever concentration variables may be used, the factor Γ is correlated to the fluctuation of chemical composition. For example, the factor Γ for the chemical relaxation of $A \rightleftarrows B$ has been given by $\Gamma_\alpha = 1/(1/\overline{\alpha} + 1/(1 - \overline{\alpha})) = \overline{\alpha}(1 - \overline{\alpha}) = K_0/(1 + K_0)^2$, where $\overline{\alpha}$ is the mole fraction of chemical species A and $K_0 = (1 - \overline{\alpha})/\overline{\alpha}$ the equilibrium constant. The factor Γ_α is consistent with $\sigma^2(\infty)/N = p_A(\infty)\{1 - p_A(\infty)\}$, if it is assumed that $p_A(\infty) = \overline{\alpha}$.

[5] K. Ishida, *J. Phys. Chem.*, **70**, 3806 (1966); **72**, 92 (1968).

$$P_{n_\mathrm{C}^{(0)}}(0) = 1,\ i.e.,\ G(\theta, 0) = \theta^{n_\mathrm{C}^{(0)}},$$

$$\begin{aligned}G(\theta, t) = {} & \{k_2(n_\mathrm{A}^{(0)} + n_\mathrm{B}^{(0)}) + k_{-2}\}^{-\frac{n_\mathrm{A}^{(0)}n_\mathrm{B}^{(0)}}{n_\mathrm{A}^{(0)}+n_\mathrm{B}^{(0)}}-n_\mathrm{C}^{(0)}} \\ & \times\{k_{-2} + k_2(n_\mathrm{A}^{(0)} + n_\mathrm{B}^{(0)})\mathrm{e}^{-t/\tau_2} \\ & +k_2(n_\mathrm{A}^{(0)} + n_\mathrm{B}^{(0)})(1 - \mathrm{e}^{-t/\tau_2})\theta\}^{\frac{n_\mathrm{A}^{(0)}n_\mathrm{B}^{(0)}}{n_\mathrm{A}^{(0)}+n_\mathrm{B}^{(0)}}} \\ & \times\{k_{-2}(1 - \mathrm{e}^{-t/\tau_2}) \\ & +[k_2(n_\mathrm{A}^{(0)} + n_\mathrm{B}^{(0)}) + k_{-2}\mathrm{e}^{-t/\tau_2}]\theta\}^{n_\mathrm{C}^{(0)}} \qquad (16)\end{aligned}$$

where $\tau_2 = \{k_2(n_\mathrm{A}^{(0)} + n_\mathrm{B}^{(0)}) + k_{-2}\}^{-1}$ is the relaxation time. Since, then, the mean number of C molecules, $\langle n_\mathrm{C}\rangle$, is given by $\theta\partial G/\partial\theta|_{\theta=1} = \langle n_\mathrm{C}\rangle$, we have as the deviation from the initial value, $\Delta\langle n_\mathrm{C}\rangle = \langle n_\mathrm{C}\rangle - n_\mathrm{C}^{(0)}$,

$$\Delta\langle n_\mathrm{C}\rangle = \frac{k_2 n_\mathrm{A}^{(0)}n_\mathrm{B}^{(0)} - k_{-2}n_\mathrm{C}^{(0)}}{k_2(n_\mathrm{A}^{(0)} + n_\mathrm{B}^{(0)}) + k_{-2}}(1 - \mathrm{e}^{-t/\tau_2}) \qquad (17)$$

By the procedure given in Appendix I, we can transform Eq. (17) into the equation involving the fluctuation of chemical species C

$$\Delta\langle n_\mathrm{C}\rangle = \sigma_\mathrm{C}^2(\infty)\left(\frac{\partial \ln K_2}{\partial Z}\right)_0 \delta Z(1 - \mathrm{e}^{-t/\tau_2}) \qquad (18)$$

which is of the same form as Eq. (11). In Eq. (18), $K_2 = k_2/k_{-2}$ is the equilibrium constant and the fluctuation for chemical species C is given by

$$\sigma_\mathrm{C}^2(\infty) = \frac{(n_\mathrm{A}^{(0)}n_\mathrm{B}^{(0)} + n_\mathrm{B}^{(0)}n_\mathrm{C}^{(0)} + n_\mathrm{C}^{(0)}n_\mathrm{A}^{(0)})K_2}{\{1 - (n_\mathrm{A}^{(0)} + n_\mathrm{B}^{(0)})K_2\}^2} \qquad (19)$$

which has been calculated by the formula

$$\sigma_\mathrm{C}^2(t) = (\theta^2\partial^2 G/\partial\theta^2 + \theta\partial G/\partial\theta)|_{\theta=1} - (\theta\partial G/\partial\theta|_{\theta=1})^2$$

When, however, it is taken into consideration that the approximation $\langle n_\mathrm{C}\rangle^2{}_\infty - n_\mathrm{C}^{(0)2} \ll n_\mathrm{A}^{(0)}n_\mathrm{B}^{(0)} + n_\mathrm{B}^{(0)}n_\mathrm{C}^{(0)} + n_\mathrm{C}^{(0)}n_\mathrm{A}^{(0)}$ holds for the chemical relaxation we are concerned with, Eq. (19) can be transformed into the form of the factor Γ of Eigen - de Maeyer,

$$\sigma_\mathrm{C}^2(\infty) = (1/\langle n_\mathrm{A}\rangle_\infty + 1/\langle n_\mathrm{B}\rangle_\infty + 1/\langle n_\mathrm{C}\rangle_\infty)^{-1} \qquad (20)$$

where $\langle n_\mathrm{A}\rangle_\infty = n_\mathrm{A}^{(0)} - (\langle n_\mathrm{C}\rangle_\infty - n_\mathrm{C}^{(0)})$ and $\langle n_\mathrm{B}\rangle_\infty = n_\mathrm{B}^{(0)} - (\langle n_\mathrm{C}\rangle_\infty - n_\mathrm{C}^{(0)})$. We thus see from Eqs. (11) and (18) that the stochastic theory of chemical relaxation may make it possible to evaluate the fluctuation of chemical composition.

Two-step Reaction

Up to the present, we have stochastically discussed only the chemical relaxations of one-step reactions, but we must also investigate along the same line as in the preceding section how the fluctuation of chemical composition appears in the chemical relaxation of multiple-step reaction. For instance, we can take up a two-step reaction $\mathrm{A} \rightleftharpoons \mathrm{B} \rightleftharpoons \mathrm{C}$. For practical purposes, however, we are interested in the reaction such as $\mathrm{A}+\mathrm{B} \rightleftharpoons \mathrm{C} \rightleftharpoons \mathrm{D}$.

It is necessary to write down the equation describing the stochastic process for the chemical relaxation of this reaction. Let us denote by $n_\mathrm{A}^{(0)}$, $n_\mathrm{B}^{(0)}$, $n_\mathrm{C}^{(0)}$ and $n_\mathrm{D}^{(0)}$ the numbers of A, B, C and D molecules present in the initial equilibrium system, respectively. If the changes of the numbers of A (and B), C and D molecules from the equilibrium values due to the change of an external state variable Z are chosen as the random variables, which assume the realized values x, y and z at time t, the joint probability distribution $P_{x,y,z}(t)$ satisfies the linear equation similar to Eq. (15′)

$$\begin{aligned}\mathrm{d}P_{x,y,z}(t)/\mathrm{d}t = {} & \\ & \kappa_1\{n_\mathrm{A}^{(0)}n_\mathrm{B}^{(0)} + (n_\mathrm{A}^{(0)} + n_\mathrm{B}^{(0)})(x+1)\}P_{x+1,y-1,z}(t) \\ & +\kappa_{-1}(n_\mathrm{C}^{(0)} + y + 1)P_{x-1,y+1,z}(t) \\ & -\{\kappa_1(n_\mathrm{A}^{(0)}n_\mathrm{B}^{(0)} + (n_\mathrm{A}^{(0)} + n_\mathrm{B}^{(0)})x) \\ & +(\kappa_{-1} + \kappa_2)(n_\mathrm{C}^{(0)} + y) + \kappa_{-2}(n_\mathrm{D}^{(0)} + z)\}P_{x,y,z}(t) \\ & +\kappa_2(n_\mathrm{C}^{(0)} + y + 1)P_{x,y+1,z-1}(t) \\ & +\kappa_{-2}(n_\mathrm{D}^{(0)} + z + 1)P_{x,y-1,z+1}(t) \qquad (21)\end{aligned}$$

where κ_1 and κ_{-1} are the transition probabilities for the forward and reverse reactions of $\mathrm{A}+\mathrm{B} \rightleftharpoons \mathrm{C}$ and similarly κ_2 and κ_{-2} the transition probabilities for $\mathrm{C} \rightleftharpoons \mathrm{D}$. Defining the generating function $P_{x,y,z}(t)$ by

$$G(\theta_1, \theta_2, \theta_3;\, t) = \sum_{x,y,z=0}^{\infty} \theta_1^x\theta_2^y\theta_3^z P_{x,y,z}(t)$$

we obtain, from Eq. (21),

$$\begin{aligned}\frac{\partial G}{\partial t} = {} & -\kappa_1(n_\mathrm{A}^{(0)} + n_\mathrm{B}^{(0)})(\theta_1 - \theta_2)\frac{\partial G}{\partial\theta_1} \\ & +\{\kappa_{-1}\theta_1 - (\kappa_{-1} + \kappa_2)\theta_2 + \kappa_2\theta_3\} \\ & \times\frac{\partial G}{\partial\theta_2} + \kappa_{-2}(\theta_2 - \theta_3)\frac{\partial G}{\partial\theta_3} \\ & -\{\kappa_1 n_\mathrm{A}^{(0)}n_\mathrm{B}^{(0)}(1 - \theta_2/\theta_1) + \kappa_{-1}n_\mathrm{C}^{(0)}(1 - \theta_1/\theta_2) \\ & +\kappa_2 n_\mathrm{C}^{(0)}(1 - \theta_3/\theta_2) + \kappa_{-2}n_\mathrm{D}^{(0)}(1 - \theta_2/\theta_3\}G\end{aligned}$$

This partial differential equation is to be solved with the initial condition $G(\theta_1, \theta_2, \theta_3; 0) = 1$, which means that $P_{0,0,0}(0) = 1$. The solution can be written in the form

$$\begin{aligned}G(\theta_1, \theta_2, \theta_3;\, t) = {} & \theta_1^{-\frac{n_\mathrm{A}^{(0)}n_\mathrm{B}^{(0)}}{n_\mathrm{A}^{(0)}+n_\mathrm{B}^{(0)}}}\theta_2^{-n_\mathrm{C}^{(0)}}\theta_3^{-n_\mathrm{D}^{(0)}} \\ & \times\left\{\sum_{i=1}^{3} p_i(t)\theta_i\right\}^{\frac{n_\mathrm{A}^{(0)}n_\mathrm{B}^{(0)}}{n_\mathrm{A}^{(0)}+n_\mathrm{B}^{(0)}}}\left\{\sum_{i=1}^{3} q_i(t)\theta_i\right\}^{n_\mathrm{C}^{(0)}} \\ & \times\left\{\sum_{i=1}^{3} r_i(t)\theta_i\right\}^{n_\mathrm{D}^{(0)}} \qquad (22)\end{aligned}$$

where $p_i(t)$, $q_i(t)$ and $r_i(t)$ will be given in Appendix II.

For the sake of simplicity, we restrict ourselves to investigate how the change of the number of D molecules in the relaxing system can be related to the fluctuation. From Eq. (22), we obtain as the expected value

$$\langle z\rangle = \frac{n_\mathrm{A}^{(0)}n_\mathrm{B}^{(0)}}{n_\mathrm{A}^{(0)}+n_\mathrm{B}^{(0)}}p_3(t) + n_\mathrm{C}^{(0)}q_3(t) + n_\mathrm{D}^{(0)}\{r_3(t) - 1\} \qquad (23)$$

where we have used $(\theta_3\partial G/\partial\theta_3)|_{\theta_1=\theta_2=\theta_3=1} = \langle z\rangle$. If the equilibriation in the first stage is much faster than in the second, it follows that $\kappa_1(n_\mathrm{A}^{(0)} + n_\mathrm{B}^{(0)})$ and

κ_{-1} are sufficiently large compared with κ_2 and κ_{-2}. We then have the inequality $\alpha \gg \beta$ and the approximations

$$\alpha = \kappa_1(n_A^{(0)} + n_B^{(0)}) + \kappa_{-1}$$

and

$$\beta = \frac{\kappa_1(n_A^{(0)} + n_B^{(0)}))\kappa_2}{\kappa_1(n_A^{(0)} + n_B^{(0)}) + \kappa_{-1}} + \kappa_{-2}$$

In such a case, Eq. (23) may be written as

$$\langle z \rangle = \left\{ \frac{n_A^{(0)} n_B^{(0)}}{n_A^{(0)} + n_B^{(0)}} + n_C^{(0)} - n_D^{(0)} \frac{\kappa_{-2}\alpha}{\kappa_1(n_A^{(0)} + n_B^{(0)})\kappa_2} \right\} \times \frac{\kappa_1(n_A^{(0)} + n_B^{(0)})\kappa_2}{\alpha\beta}(1 - \mathrm{e}^{-t/\tau_2}) \tag{24}$$

where $\tau_2 = \beta^{-1}$ denotes the relaxation time. If, however, we introduce the equilibrium constants $\kappa_1/\kappa_{-1} = K_1$, $\kappa_2/\kappa_{-2} = K_2$, $n_C^{(0)}/n_A^{(0)} n_B^{(0)} = K_1^{(0)}$ and $n_D^{(0)}/n_C^{(0)} = K_2^{(0)}$, we obtain, by the same procedure as in the transformation from Eq. (17) to Eq. (18)

$$\langle z \rangle = \sigma_D^2(\infty) \left\{ 1 + \frac{n_A^{(0)} n_B^{(0)}}{n_A^{(0)} n_B^{(0)} + n_B^{(0)} n_C^{(0)} + n_C^{(0)} n_A^{(0)}} \times \frac{(\partial \ln K_1/\partial Z)_0}{(\partial \ln K_2/\partial Z)_0} \right\} (\partial \ln K_2/\partial Z)_0 \delta Z (1 - \mathrm{e}^{-t/\tau_2}) \tag{25}$$

where the fluctuation $\sigma_D^2(\infty)$ for chemical species D in the new chemical equilibrium state is given by

$$\sigma_D^2(\infty) = \left\{ \frac{n_A^{(0)} n_B^{(0)}}{n_A^{(0)} + n_B^{(0)}} + n_C^{(0)} + n_D^{(0)} \right\} \times \frac{\kappa_1(n_A^{(0)} + n_B^{(0)})\kappa_2}{\alpha\beta} \left\{ 1 - \frac{\kappa_1(n_A^{(0)} + n_B^{(0)})\kappa_2}{\alpha\beta} \right\}$$

Since the first stage of the reaction is considered to be in stationary state, it may be expected that

$$|(\partial \ln K_1/\partial Z)_0/(\partial \ln K_2/\partial Z)_0| = |n_D^{(0)}/(n_C^{(0)} + n_D^{(0)})|$$

It is then concluded that Eq. (25) is reduced to

$$\langle z \rangle = \sigma_D^2(\infty)(\partial \ln K_2/\partial Z)_0 \partial Z (1 - \mathrm{e}^{-t/\tau_2}) \tag{26}$$

which is of the same form as Eqs. (11) and (18).

We can in general say that chemical relaxation should be accompanied with the fluctuation of chemical composition.

Appendix I

The first member on the right-hand side of Eq. (17) can be written in the form

$$\frac{k_2 n_A^{(0)} n_B^{(0)} - k_{-2} n_C^{(0)}}{k_2(n_A^{(0)} + n_B^{(0)}) + k_{-2}} = \sigma_C^2(\infty)(K_2 - K_2^{(0)}) \times \frac{n_A^{(0)} n_B^{(0)} \{(n_A^{(0)} + n_B^{(0)})K_2 + 1\}}{(n_A^{(0)} n_B^{(0)} + n_B^{(0)} n_C^{(0)} + n_C^{(0)} n_A^{(0)})K_2} \tag{A.1}$$

where the fluctuation (19) and the equilibrium constants $n_C^{(0)}/n_A^{(0)} n_B^{(0)} = K_2^{(0)}$ and $k_2/k_{-2} = K_2$ have been used. If we apply $K_2 = K_2^{(0)}\{1 + (\partial \ln K_2/\partial Z)_0 \delta Z\}$ to Eq. (A.1), we have, by neglecting the terms of higher order than the first of δZ,

$$\frac{k_2 n_A^{(0)} n_B^{(0)} - k_{-2} n_C^{(0)}}{k_2(n_A^{(0)} + n_B^{(0)}) + k_{-2}} = \sigma_C^2(\infty) \left(\frac{\partial \ln K_2}{\partial Z} \right)_0 \delta Z \times \left\{ 1 - \frac{n_A^{(0)} n_B^{(0)}}{n_A^{(0)} n_B^{(0)} + n_B^{(0)} n_C^{(0)} + n_C^{(0)} n_A^{(0)}} \left(\frac{\partial \ln K_2}{\partial Z} \right)_0 \delta Z \right\} \simeq \sigma_C^2(\infty) \left(\frac{\partial \ln K_2}{\partial Z} \right)_0 \delta Z \tag{A.2}$$

since it is necessary that $1 \gg |(\partial \ln K_2/\partial Z)_0 \delta Z| > 0$ for the linearization such as Eq. (15′).[6] We thus obtain Eq. (18) from Eq. (17).

Appendix II

In Eq. (22), $p_i(t)$, $q_i(t)$ and $r_i(t)$ $(i=1, 2, 3)$ have the following expressions:

$$p_1(t) = \frac{\kappa_{-1}\kappa_{-2}}{\alpha\beta} - \frac{\kappa_1(n_A^{(0)} + n_B^{(0)})(\kappa_2 + \kappa_{-2} - \alpha)}{\alpha(\alpha - \beta)}\mathrm{e}^{-\alpha t} + \frac{\kappa_1(n_A^{(0)} + n_B^{(0)})(\kappa_2 + \kappa_{-2} - \beta)}{\beta(\alpha - \beta)}\mathrm{e}^{-\beta t}$$

$$p_2(t) = \frac{\kappa_1(n_A^{(0)} + n_B^{(0)})\kappa_{-2}}{\alpha\beta} + \frac{\kappa_1(n_A^{(0)} + n_B^{(0)})(\kappa_{-2} - \alpha)}{\alpha(\alpha - \beta)}\mathrm{e}^{-\alpha t} - \frac{\kappa_1(n_A^{(0)} + n_B^{(0)})(\kappa_{-2} - \beta)}{\beta(\alpha - \beta)}\mathrm{e}^{-\beta t}$$

$$p_3(t) = \frac{\kappa_1(n_A^{(0)} + n_B^{(0)})\kappa_2}{\alpha\beta} + \frac{\kappa_1(n_A^{(0)} + n_B^{(0)})\kappa_2}{\alpha(\alpha - \beta)}\mathrm{e}^{-\alpha t} - \frac{\kappa_1(n_A^{(0)} + n_B^{(0)})\kappa_2}{\beta(\alpha - \beta)}\mathrm{e}^{-\beta t}$$

$$q_1(t) = \frac{\kappa_{-1}\kappa_{-2}}{\alpha\beta} + \frac{\kappa_{-1}(\kappa_{-2} - \alpha)}{\alpha(\alpha - \beta)}\mathrm{e}^{-\alpha t} - \frac{\kappa_{-1}(\kappa_{-2} - \beta)}{\beta(\alpha - \beta)}\mathrm{e}^{-\beta t}$$

$$q_2(t) = \frac{k_1(n_A^{(0)} + n_B^{(0)})\kappa_{-2}}{\alpha\beta} - \frac{\kappa_1(n_A^{(0)} + n_B^{(0)})\kappa_2 + \kappa_{-1}\kappa_{-2} - (\kappa_{-1} + \kappa_2)\alpha}{\alpha(\alpha - \beta)}\mathrm{e}^{-\alpha t} + \frac{\kappa_1(n_A^{(0)} + n_B^{(0)})\kappa_2 + \kappa_{-1}\kappa_{-2} - (\kappa_{-1} + \kappa_2)\beta}{\beta(\alpha - \beta)}\mathrm{e}^{-\beta t}$$

$$q_3(t) = \frac{\kappa_1(n_A^{(0)} + n_B^{(0)})\kappa_2}{\alpha\beta} + \frac{\kappa_2(\kappa_1(n_A^{(0)} + n_B^{(0)}) - \alpha)}{\alpha(\alpha - \beta)}\mathrm{e}^{-\alpha t} - \frac{\kappa_2(\kappa_1(n_A^{(0)} + n_B^{(0)}) - \beta)}{\beta(\alpha - \beta)}\mathrm{e}^{-\beta t}$$

and

$$r_1(t) = \frac{\kappa_{-1}\kappa_{-2}}{\alpha\beta} + \frac{\kappa_{-1}\kappa_{-2}}{\alpha(\alpha - \beta)}\mathrm{e}^{-\alpha t} - \frac{\kappa_{-1}\kappa_{-2}}{\beta(\alpha - \beta)}\mathrm{e}^{-\beta t}$$

$$r_2(t) = \frac{\kappa_1(n_A^{(0)} + n_B^{(0)})\kappa_{-2}}{\alpha\beta} + \frac{\kappa_{-2}(\kappa_1(n_A^{(0)} + n_B^{(0)}) - \alpha)}{\alpha(\alpha - \beta)}\mathrm{e}^{-\alpha t} - \frac{\kappa_{-2}(\kappa_1(n_A^{(0)} + n_B^{(0)}) - \beta)}{\beta(\alpha - \beta)}\mathrm{e}^{-\beta t}$$

$$r_3(t) = \frac{\kappa_1(n_A^{(0)} + n_B^{(0)})\kappa_2}{\alpha\beta} + \frac{\kappa_{-2}(\kappa_2 + \kappa_{-2} - \beta)}{\alpha(\alpha - \beta)}\mathrm{e}^{-\alpha t} - \frac{\kappa_{-2}(\kappa_2 + \kappa_{-2} - \alpha)}{\beta(\alpha - \beta)}\mathrm{e}^{-\beta t}$$

where α and β $(\alpha > \beta > 0)$ are the roots of the equation

$$\eta^2 - \{\kappa_1(n_A^{(0)} + n_B^{(0)}) + \kappa_{-1} + \kappa_2 + \kappa_{-2}\}\eta + \kappa_1(n_A^{(0)} + n_B^{(0)})(\kappa_2 + \kappa_{-2}) + \kappa_{-1}\kappa_{-2} = 0$$

and $\sum_{i=1}^{3} p_i(t) = \sum_{i=1}^{3} q_i(t) = \sum_{i=1}^{3} r_i(t) = 1$ and $p_i(\infty) = q_i(\infty) = r_i(\infty)$ are satisfied.

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6) G. H. Czerlinski, "Chemical Relaxation," Marcel Dekker Inc., New York, N. Y. (1966), p. 27.