

Theory of Bimolecular Reaction Processes in Liquids

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A theoretical approach to the problem of diffusion controlled bimolecular reactions is presented. In order to take into account the time correlation of reaction process of our many-particle system, the probability of the first reaction is introduced as a fundamental quantity. Time development of the ensemble of our system is formulated using the probability of the first reaction. An approximation which reduces the general formula to a problem of Markov process is adopted. Then it is shown that, if we assume stationary reaction rate, the usual phenomenological kinetic equation, i.e. the so called law of mass action can be derived as the first order approximation, and as the second order approximation the deviation from the law of mass action is examined. For the general case, in order to obtain the probability of the first reaction in an explicit form, it becomes necessary to solve the multi-dimensional diffusion equation with pair absorbing interactions, which is calculated using the binary collision expansion method.

§ 1. Introduction

Diffusion controlled reaction processes have been widely known, for example, coagulation of colloidal particles, quenching of fluorescence, excitation transfers and usual bimolecular reactions of the type $A + B \rightarrow AB$. Theoretical investigations have been developed by many authors,¹⁾⁻¹¹⁾ since Smoluchowski's fundamental work, which was originally developed to explain the process of coagulation of colloids, appeared. Many of these works were devoted to deriving formulae for collision frequency or reaction rate as a function of time and friction constant, on the basis of Smoluchowski's equation. Assuming the independence of collisions, they solved essentially two-body problems under various boundary and initial conditions.

If we consider the reaction process as a time dependent many-body problem, it becomes necessary to take into account complicated spatial and time correlations. The effects of these correlations have been also discussed by several authors. However, the systematic formulation has seemingly not yet been established. The purpose of this paper is to derive a general formula which describes the time development of an ensemble of our many-particle system, and investigate the effects of these correlations on the reaction rates.

In order to take into account the time correlations of reaction process, the probability of the first reaction is introduced as a fundamental quantity. By using this probability function, time development of the ensemble of our system is formulated in the most general form in § 2. On the assumption of the uniform

spatial distribution for the initial ensemble, the problem is reduced to that of Markov process whose mathematical properties are discussed in § 3. In §§ 4 and 5, by assuming the stationary reaction rate, the usual phenomenological kinetic equation, i. e. the law of mass action is derived as the first order approximation, and by investigating the second order approximation the deviations from the law of mass action are discussed. In order to have an explicit result, it is necessary to calculate the probability of the first reaction by solving the multi-dimensional diffusion equation with pair absorbing interactions, which has just the same form as the Bloch equation for the density matrix of many-body system which is discussed in § 6. Finally §§ 7 and 8 are devoted to the calculation of this multi-dimensional diffusion equation, using the binary collision expansion method which were formerly developed for many-body problems.

§ 2. Mathematical formulation

Let us consider a solution containing two kinds of particles (A and B) as solutes, and suppose that these particles undergo random motions described by diffusion constants D_A and D_B respectively and also A particle reacts with B particle at a relative distance r with the definite probability $v(r)$, forming a complex AB. In the following discussion it is assumed that the reaction is irreversible and also direct interactions between particles of the same type, which may give some modifications to random motion, can be neglected.

As an initial ensemble, we consider an ensemble of those systems in which N particles of type A and M particles of type B are distributed in a medium of volume V and no complex AB is formed at $t=0$. These particles begin random diffusive motions and when any A particle approaches any B particle within the reaction range, reactions of the type $A+B \rightarrow AB$ will start. Thus we shall denote by $W_{N-n,N}(t)$ the probability that at a time t , n AB complexes have already formed, so that $N-n$ particles of type A and $M-n$ particles of type B remain unreacted.

Using this probability function, the averaged density of A particles at time t is given by

$$C_A(t) = V^{-1} \sum_{n=0}^N (N-n) W_{N-n,N}(t). \quad (2.1)$$

In order to take into account the time correlations of the reaction processes of our many-particle system, we shall introduce the probability of the first reaction $T_{N-1,N}^{i,j}(X, Y; t|X_0, Y_0; t_0)$ defined as follows. $X = (x_1, x_2, \dots, x_N)$ is a set of coordinates of N particles of type A and x_i is a position vector (in general it may include the coordinates of internal freedom) of the i -th A particle, $Y = (y_1, y_2, \dots, y_M)$ is the same for B particles. The probability of the first reaction $T_{N-1,N}^{i,j}(X, Y; t|X_0, Y_0; t_0) dX dY dt$ is the probability that until time t no reaction has occurred and $N+M$ particles of types A and B which have started from the initial positions (X_0, Y_0) are found in the volume element $dX dY$ at the

positions (X, Y) at time t and in the time interval from t to $t+dt$ the first reaction occurs between the i -th A particle and the j -th B particle at the positions x_i and y_j respectively.

Apparently the probability of the first reaction can be expressed in the form

$$\begin{aligned} & T_{N-1, N}^{i, j}(X, Y; t|X_0, Y_0; t_0) dX dY dt \\ &= v(x_i, y_j) P(X, Y; t|X_0, Y_0; t_0) dX dY dt, \end{aligned} \quad (2.2)$$

where $v(x_i, y_j)$ is the absolute reaction rate defined above and assumed to be a function of the relative distance $|x_i - y_j|$. $P(X, Y; t|X_0, Y_0; t_0) dX dY$ is the probability that $N+M$ particles of types A and B, which started from the positions (X_0, Y_0) at time t_0 , still not reacted and are found in the volume element $dX dY$ at the positions (X, Y) at time t . In the present formulation the processes that two or more AB pairs react at the same instant are neglected. Then the probability that n AB pairs are found at time t , $W_{N-n, N}(t)$, can be constructed by summing up the probabilities of each individual process of successive reactions of n AB pairs. Actually it can be written in the form

$$\begin{aligned} W_{N-n, N}(t) &= \int_0^t dt_n \int_0^{t_n} dt_{n-1} \cdots \int_0^{t_2} dt_1 \int dX dY \int dX_n dY_n \cdots \int dX_0 dY_0 \\ &\times \sum_{\{(i_k, j_k)\}} P(X/(i_1 \cdots i_n), Y/(j_1 \cdots j_n); t|X_n/(i_1 \cdots i_n), Y_n/(j_1 \cdots j_n); t_n) \\ &\times T_{N-n, N-n+1}^{i_n, j_n}(X_n/(i_1 \cdots i_{n-1}), Y_n/(j_1 \cdots j_{n-1}); t_n| \\ &\quad X_{n-1}/(i_1 \cdots i_{n-1}), Y_{n-1}/(j_1 \cdots j_{n-1}); t_{n-1}) \\ &\times T_{N-n+1, N-n+2}^{i_{n-1}, j_{n-1}}(X_{n-1}/(i_1 \cdots i_{n-2}), Y_{n-1}/(j_1 \cdots j_{n-2}); t_{n-1}| \\ &\quad X_{n-2}/(i_1 \cdots i_{n-2}), Y_{n-2}/(j_1 \cdots j_{n-2}); t_{n-2}) \\ &\times \cdots \cdots \cdots \\ &\times T_{N-1, N}^{i_1, j_1}(X_1, Y_1; t_1|X_0, Y_0; t_0) \cdot f(X_0, Y_0), \end{aligned} \quad (2.3)$$

where the notations $X_k/(i_1 \cdots i_\nu)$ and $Y_k/(j_1 \cdots j_\nu)$ denote the coordinates of $N-\nu$ particles of type A and $M-\nu$ particles of type B at time t_k respectively, excluding the coordinates of i_1, \cdots, i_ν -th particles of type A ($x_{i_1}, \cdots, x_{i_\nu}$) and j_1, \cdots, j_ν -th particles of type B ($y_{j_1}, \cdots, y_{j_\nu}$) which have already reacted. The summation is taken over all the possible sequences of n different AB pairs $(i_1, j_1), (i_2, j_2), \cdots, (i_n, j_n)$, where $i_\nu = 1, 2, \cdots, N$, $j_\nu = 1, 2, \cdots, M$ and $i_\nu \neq i_\mu, j_\nu \neq j_\mu$ for $\nu \neq \mu$. $f(X_0, Y_0)$ is the distribution function of particles for the initial ensemble.

Expression (2.3) gives a detailed information of the reaction process of our system and the space and time correlations of the process are completely included in that complicated integration. However, calculation of Eq. (2.3) is

actually almost impossible, so it is necessary to reduce the equation to a more simple form by using some suitable approximations.

§ 3. Formulation as a Markov process

If, at the initial time, the particles A and B are uniformly distributed in the medium of volume V , then the chance of reaction of the AB pair can be expected uniformly in the space. In this case, we can reduce the problem to a problem of the Markov process by assuming that at each instant t_k just after the k -th reaction has occurred remaining unreacted particles have uniform distribution. That is, under this assumption, the multiple integration of space coordinates in Eq. (2.3) can be performed independently, and we have

$$\begin{aligned} W_{N-n,N}(t) &= \int_0^t dt_1 W_{N-n,N-1}(t-t_1) T_{N-1,N}(t_1) \\ &= \int_0^t dt_n \int_0^{t_n} dt_{n-1} \cdots \int_0^{t_2} dt_1 W_{N-n,N-n}(t-t_n) \\ &\quad \times T_{N-n,N-n+1}(t_n-t_{n-1}) T_{N-n+1,N-n+2}(t_{n-1}-t_{n-2}) \\ &\quad \times \cdots T_{N-1,N}(t_1), \\ &\quad \text{for } n \geq 1, \end{aligned} \quad (3.1)$$

or using a simple notation for the convolutions

$$W_{N-n,N}(t) = W_{N-n,N-n} * T_{N-n,N-n+1} * T_{N-n+1,N-n+2} * \cdots * T_{N-1,N}, \quad (3.1')$$

where $T_{N-k-1,N-k}(\tau)$ is the probability that at the initial time $N-k$ particles of type A and $M-k$ particles of type B are uniformly distributed in the medium of volume V and in the time interval from τ to $\tau+d\tau$ the first reaction occurs between one of the AB pairs, and $W_{N-k,N-k}(\tau)$ is the probability that $N-k$ A particles and $M-k$ B particles with uniform initial distribution remain unreacted until time τ . Apparently these probability functions are given by

$$W_{N-k,N-k}(t) = \int P(X, Y; t | X_0, Y_0; 0) f(X_0, Y_0) dX_0 dY_0 dX dY, \quad (3.2)$$

$$T_{N-k-1,N-k}(t) = \sum_{i,j} \int v(x_i, y_j) P(X, Y; t | X_0, Y_0; 0) f(X_0, Y_0) dX_0 dY_0 dX dY, \quad (3.3)$$

where X_0 and X stand for the coordinates of $N-k$ particles of type A, and Y_0 and Y the coordinates of $M-k$ particles of type B. Because of the Markovian approximation, in Eqs. (3.2) and (3.3) it becomes unnecessary to distinguish the particles as we have done in Eq. (2.3) by writing the arguments with fractional coordinates.

Owing to the normalization condition of the probabilities, it is clear that

$$\int_0^t T_{N-k-1, N-k}(t') dt' + W_{N-k, N-k}(t) = 1,$$

or in a differential form

$$T_{N-k-1, N-k}(t) = -dW_{N-k, N-k}(t)/dt. \quad (3.4)$$

Thus, if we can obtain an explicit form of the distribution function $P(X, Y; t|X_0, Y_0; 0)$, the probability of the first reaction $T_{N-k-1, N-k}(t)$ is given by calculating Eqs. (3.2) and (3.4); then using Eq. (3.1) and finally Eq. (2.1) we can evaluate the averaged density of A particles $C_A(t)$ as a function of time.

Here we shall denote the Laplace transform of a function $F(t)$ by

$$L(F; s) = \int_0^\infty F(t) e^{-st} dt. \quad (3.5)$$

Then, from Eq. (3.4) we get

$$L(T_{N-k-1, N-k}; s) = sL(1 - W_{N-k, N-k}; s), \quad (3.6)$$

and the Laplace transform of Eq. (3.1) becomes

$$\begin{aligned} L(W_{N-n, N}; s) &= L(W_{N-n, N-n}; s) s^n \prod_{k=0}^{n-1} L(1 - W_{N-k, N-k}; s) \\ &= F_{n-1}(s) - F_n(s), \quad \text{for } n \geq 1, \end{aligned} \quad (3.7)$$

where

$$F_n(s) = s^n \prod_{k=0}^n L(1 - W_{N-k, N-k}; s), \quad \text{for } n \geq 0. \quad (3.8)$$

From the obvious relation

$$L(W_{N, N}; s) = \frac{1}{s} - L(1 - W_{N, N}; s),$$

it is seen that we can also use the formula (3.7) for $n=0$ by using the definition

$$F_{-1} = 1/s. \quad (3.9)$$

Thus we can obtain the Laplace transform of the averaged density of A particles, using Eq. (2.1):

$$\begin{aligned} L(C_A; s) &= V^{-1} \sum_{n=0}^N (N-n) L(W_{N-n, N}; s) \\ &= V^{-1} \sum_{n=0}^N (N-n) (F_{n-1}(s) - F_n(s)) \\ &= C_A^0 \left\{ \frac{1}{s} - \frac{1}{N} \sum_{n=0}^{N-1} F_n(s) \right\}, \end{aligned} \quad (3.10)$$

where $C_A^0 = N/V$ is the initial value of the density $C_A(t)$.

Finally, the inverse transformation of Eq. (3.10) gives

$$C_A(t) = C_A^0 \left\{ 1 - \frac{1}{N} \sum_{n=0}^{N-1} L^{-1}(F_n; t) \right\}, \quad (3.11)$$

where L^{-1} denotes the inverse Laplace transformation.

§ 4. Elementary kinetic equation of stationary reaction rate

From Eq. (3.1) we have

$$\begin{aligned} \frac{d}{dt} W_{N-n,N}(t) &= \int_0^t dt_{n-1} \int_0^{t_{n-1}} dt_{n-2} \cdots \int_0^{t_2} dt_1 T_{N-n,N-n+1}(t-t_{n-1}) \\ &\quad \times T_{N-n+1,N-n+2}(t_{n-1}-t_{n-2}) \cdots T_{N-1,N}(t_1) \\ &\quad - \int_0^t dt_n \int_0^{t_n} dt_{n-1} \cdots \int_0^{t_2} dt_1 T_{N-n-1,N-n}(t-t_n) \\ &\quad \times T_{N-n,N-n+1}(t_n-t_{n-1}) \cdots T_{N-1,N}(t_1), \end{aligned} \quad (4.1)$$

where in the second term the relation (3.4) is used.

Now we shall define the rate function $K_{N-k}(t)$ by the equation

$$K_{N-k}(t) = \frac{T_{N-k-1,N-k}(t)}{W_{N-k,N-k}(t)} = - \frac{d}{dt} \log W_{N-k,N-k}(t). \quad (4.2)$$

The rate function $K_{N-k}(t)dt$ is the conditional probability that the first reaction occurs during the time interval t and $t+dt$ when $N-k$ A particles and $M-k$ B particles remain unreacted until time t . Here, if we can assume that this rate function is independent of t and also has a form

$$K_{N-k} = \kappa(N-k)(M-k), \quad (4.3)$$

then, by using Eqs. (4.2), (4.3) and (3.1), Eq. (4.1) can be reduced to a differential equation

$$\frac{d}{dt} W_{N-n,N} = \kappa(N-n+1)(M-n+1) W_{N-n+1,N} - \kappa(N-n)(M-n) W_{N-n,N}. \quad (4.4)$$

This equation was already investigated by Rényi,^{(12),(13)} and, as shown in Appendix I, we can obtain an exact solution, which is also compared with our general formula developed in § 3. However, in application it is of interest to determine the averaged density $C_A(t)$.

We shall rewrite $W_{N-n,N}$ simply as W_m putting $m = N-n$, then we have

$$\frac{d}{dt} W_m = \kappa(m+1)(m+1+M-N) W_{m+1} - \kappa m(m+M-N) W_m, \quad (4.5)$$

and also Eq. (2.1) can be written as

$$C_A(t) = V^{-1} \sum_{m=0}^N m W_m(t) = V^{-1} \langle m \rangle. \quad (4.6)$$

Here it should be noted that if one puts $W_{N+1}=0$, Eq. (4.5) becomes applicable for W_N as well.

Thus, from Eqs. (4.5) and (4.6), we obtain

$$\frac{d}{dt} \langle m \rangle = -\kappa [\langle m^2 \rangle + (M-N) \langle m \rangle]. \quad (4.7)$$

In order to solve this equation we need the equation from which the second moment $\langle m^2 \rangle$ can be calculated. This procedure, however, leads to the hierarchy of equations which involve successively higher order moments. As the first order approximation, if we put

$$\langle m^2 \rangle = \langle m \rangle^2, \quad (4.8)$$

Eq. (4.7) becomes

$$\frac{d}{dt} C_A = -\nu [C_A + (C_B^0 - C_A^0)] C_A, \quad (4.9)$$

where $\nu = V\kappa$, $C_A^0 = N/V$ and $C_B^0 = M/V$. Equation (4.9) is the usual phenomenological kinetic equation of bimolecular reactions, the so-called law of mass action. The solution of Eq. (4.9) which satisfies the initial condition $C_A(0) = C_A^0$, is given by

$$C_A(t) = \frac{C_B^0 - C_A^0}{C_B^0 \exp[\nu(C_B^0 - C_A^0)t] - C_A^0} C_A^0. \quad (4.10)$$

In particular when $C_B^0 \gg C_A^0$, we have simply

$$C_A(t) = C_A^0 \exp(-\nu C_B^0 t). \quad (4.11)$$

Thus it has been shown that in the first order approximation our formula leads to phenomenological kinetic equations of bimolecular reactions.

§ 5. Deviations from the first order approximation

Here we shall consider a second order approximation and examine the fluctuation of density as a function of time. From Eq. (4.5) we can obtain the equation for the second order moment $\langle m^2 \rangle$,

$$\frac{d}{dt} \langle m^2 \rangle = -2\kappa \langle m^3 \rangle + \kappa \{1 - 2(M-N)\} \langle m^2 \rangle + \kappa(M-N) \langle m \rangle. \quad (5.1)$$

In order to close the equations by taking into account the second order moment, we must express the third order moment $\langle m^3 \rangle$ in Eq. (5.1) approximately using lower order moments. As a reasonable approximation, here we shall

assume a symmetric distribution for W_m , for example a normal distribution function (see Appendix I):

$$W_m = \frac{1}{\sqrt{2\pi}\sigma} \exp[-(m - \langle m \rangle)^2 / 2\sigma^2],$$

$$\sigma^2 = \langle m^2 \rangle - \langle m \rangle^2. \quad (5.2)$$

Then we can readily obtain

$$\langle m^3 \rangle = 3\langle m^2 \rangle \langle m \rangle - 2\langle m \rangle^3. \quad (5.3)$$

Hence, from Eqs. (5.1) and (5.3), we obtain

$$\frac{d}{dt} \langle m^2 \rangle = -\kappa \{6\langle m \rangle + 2(M - N) - 1\} \langle m^2 \rangle + \kappa \langle m \rangle \{4\langle m \rangle^2 + (M - N)\}, \quad (5.4)$$

or from Eqs. (4.7) and (5.4) we have

$$\frac{d}{dt} \sigma^2 = -2\kappa \{(M - N) + 2\langle m \rangle\} \sigma^2 + \kappa \{(M - N)\langle m \rangle + \langle m^2 \rangle\}. \quad (5.5)$$

Thus Eqs. (4.7) and (5.4) (or (5.5)) form a closed set of kinetic equations of the second order approximation. However, the exact solution of these equations cannot be simply calculated, so in this section let us consider two special cases which seem to be physically significant.

First we shall consider the case that $M \gg N$; then Eq. (5.5) may be written as

$$\frac{d}{dt} \sigma^2 = -2\kappa M \sigma^2 + \kappa M \langle m \rangle. \quad (5.6)$$

Solving this equation under the initial condition $\sigma^2(0) = 0$, we have

$$\sigma^2(t) = \kappa M e^{-2\kappa M t} \int_0^t e^{2\kappa M t'} \langle m \rangle dt'. \quad (5.7)$$

If we use the solution of the first order approximation (4.11), we obtain

$$\sigma^2(t) = N e^{-\kappa M t} (1 - e^{-\kappa M t}). \quad (5.8)$$

Therefore the fluctuation of the density is given by

$$\langle (m - \langle m \rangle)^2 \rangle / \langle m \rangle^2 = \frac{1}{N} (e^{\kappa M t} - 1). \quad (5.9)^*)$$

Next, let us consider another extreme case, namely $N = M$. In this case Eq. (5.5) becomes

*) $\kappa = \nu/V$ is a quantity of the order $1/V$, so $\kappa M = \nu C_B$.

$$\frac{d}{dt} \sigma^2 = -4\kappa \langle m \rangle \sigma^2 + \kappa \langle m \rangle^2, \quad (5.10)$$

where in the second term we have used the approximation $\langle m^2 \rangle = \langle m \rangle^2$. On the other hand Eq. (4.7) becomes

$$\frac{d}{dt} \langle m \rangle = -\kappa \langle m^2 \rangle, \quad (5.11)$$

whose solution of the first order approximation, namely when $\langle m^2 \rangle = \langle m \rangle^2$, is given by

$$\langle m \rangle = \frac{N}{\kappa Nt + 1}. \quad (5.12)$$

If we use Eq. (5.12), we can solve Eq. (5.10) and obtain

$$\sigma^2 = \frac{N}{3} (\kappa Nt + 1)^{-1} [1 - (\kappa Nt + 1)^{-3}], \quad (5.13)$$

so that

$$\langle (m - \langle m \rangle)^2 \rangle / \langle m \rangle^2 = \frac{1}{3N} (\kappa Nt + 1) [1 - (\kappa Nt + 1)^{-3}]. \quad (5.14)$$

In order to calculate the second order approximation of Eq. (5.11), we shall replace the right-hand side by Eq. (5.13), then we have

$$\begin{aligned} \frac{d}{dt} \langle m \rangle &= -\kappa (\langle m \rangle^2 + \sigma^2) \\ &= -\frac{\kappa N^2}{\kappa Nt + 1} \left\{ \frac{1}{\kappa Nt + 1} + \frac{1}{3N} \left[1 - \frac{1}{(\kappa Nt + 1)^3} \right] \right\}. \end{aligned} \quad (5.15)$$

Therefore, we obtain

$$\langle m \rangle = N \left[\frac{1}{\kappa Nt + 1} - \frac{1}{3N} \left\{ \log(\kappa Nt + 1) - \frac{1}{2} \left[1 - \frac{1}{(\kappa Nt + 1)^2} \right] \right\} \right] \quad (5.16)$$

or

$$C_A = C_A^0 \left[\frac{1}{\nu C_A^0 t + 1} - \frac{1}{3N} \left\{ \log(\nu C_A^0 t + 1) - \frac{1}{2} \left[1 - \frac{1}{(\nu C_A^0 t + 1)^2} \right] \right\} \right]. \quad (5.17)$$

From these results it is seen that the fluctuation of averaged density is always of the order of $N^{-1/2}$, so the deviation from the first order approximation is not important when N is sufficiently large.

§ 6. Multi-dimensional diffusion equation with pair absorbing interactions

Now we shall again go back to the main line of our discussion. In § 3 we have derived a general formula to calculate the averaged density as a func-

tion of time, where it was shown that what we need to calculate in an explicit form is the distribution function $P(X, Y; t|X_0, Y_0; t_0)$. The change of the probability distribution function P with time is due to the diffusive random motions of the particles and also the reaction processes between the AB pairs. From the definition of P , that is, the probability that all particles still have not reacted and are found at the positions (X, Y) , if we consider an inactive system in which no reactions occur, the survival probability (3.2) does not change and conserves the value unity at any time; however, when reaction processes are taken into account, obviously the survival probability decreases with time.

In general there exist the intermolecular forces which may interfere with normal diffusion processes. Diffusive motion of these particles can be described in phase space by the Fokker-Planck type equation, and when the friction constant ζ is large, a Maxwell velocity distribution will be established very soon, namely after the lapse of time of the order m/ζ ; after that time the change of space distribution function can be expected to satisfy the Smoluchowski diffusion equation characterized by the diffusion constant $D=kT/\zeta$.

Bimolecular reaction process which is assumed to be irreversible can be described by introducing the pair absorbing probability as an additional term which expresses the probability that any pair of A and B molecules disappears by forming a complex AB.

Here we assume that there exists no direct interaction between the particles, so the diffusive motions of the particles are governed by a simple diffusion equation of multi-dimensional space. Thus we have the equation

$$\begin{aligned} \frac{\partial}{\partial t} P(X, Y; t|X_0, Y_0; 0) &= \{D_A \nabla_X^2 + D_B \nabla_Y^2 - V(X, Y)\} P(X, Y; t|X_0, Y_0; 0), \\ \nabla_X^2 &= \sum_{i=1}^N \nabla_{x_i}^2, \quad \nabla_Y^2 = \sum_{j=1}^M \nabla_{y_j}^2, \\ V(X, Y) &= \sum_{i=1}^N \sum_{j=1}^M v(x_i, y_j), \end{aligned} \quad (6.1)$$

where $v(x_i, y_j)$ is the probability rate of bimolecular reaction between the i -th particle of type A and j -th particle of type B. This equation should be solved under the initial condition

$$P(X, Y; 0|X_0, Y_0; 0) = \delta(X - X_0) \delta(Y - Y_0). \quad (6.2)$$

Equation (6.1) has just the same form as the Bloch equation for the density matrix of many particles system in which $\hbar^2/2m$ and $1/kT$ correspond to the diffusion constant and the time respectively, and the Schrödinger equation for many-particle system has also the same form if we take the imaginary values of the diffusion constant and absorbing probability. Therefore, we can adopt the various techniques developed in the field of many-body problems to find the approximate solutions of Eq. (6.1). In the next section, as an example, we

shall summarize the derivation of binary collision expansion,¹⁴⁾⁻¹⁶⁾ which seems to be an adequate treatment to the present problem.

§ 7. Binary collision expansion

Simply writing the right-hand side of Eq. (6.1) by an operator \mathcal{D} , we have

$$\frac{\partial}{\partial t} P = \mathcal{D}P, \quad (7.1)$$

where

$$\begin{aligned} \mathcal{D} &= \mathcal{D}_0 - V, \\ \mathcal{D}_0 &= D_A \sum_{i=1}^N \nabla_{xi}^2 + D_B \sum_{j=1}^M \nabla_{yj}^2, \\ V &= \sum_{\alpha} v_{\alpha} = \sum_{\alpha} v(r_{\alpha}). \end{aligned} \quad (7.2)$$

In the last equation of (7.2), the pairs of A and B molecules are numbered by small Greek subscripts and the sum extends over all the AB pairs (the number of the possible AB pairs is obviously NM) and r_{α} is the relative distance of the pair α . The function P is understood to satisfy boundary conditions and the initial condition

$$P(X, Y; t_0 | X_0, Y_0; t_0) = \delta(X - X_0) \delta(Y - Y_0). \quad (7.3)$$

Now, if we consider the solution of the equation

$$\frac{\partial}{\partial t} P_{\alpha} = (\mathcal{D}_0 - v_{\alpha}) P_{\alpha} = \mathcal{D}_{\alpha} P_{\alpha} \quad (7.4)$$

with the same boundary and initial conditions, the solution P_{α} is related with the solution P by the integral equation

$$\begin{aligned} P(X, Y; t | X_0, Y_0; t_0) &= P_{\alpha}(X, Y; t | X_0, Y_0; t_0) \\ &\quad - \int_{t_0}^t dt' \int dX' dY' P(X, Y; t | X', Y'; t') (V - v_{\alpha}) \\ &\quad \times P(X', Y'; t' | X_0, Y_0; t_0). \end{aligned} \quad (7.5)$$

We shall introduce an abbreviated notation $\{A, B\}$ defined by

$$\{A, B\} = \int_{t_0}^t dt' \int dX' dY' A(X, Y; t | X', Y'; t') B(X', Y'; t' | X_0, Y_0; t_0). \quad (7.6)$$

The operation $\{A, B\}$ is associative, so that the inner parentheses can be omitted:

$$\{\{A, B\}, C\} = \{A, \{B, C\}\} = \{A, B, C\}. \quad (7.7)$$

In this notation Eq. (7.5) is written as

$$P = P_\alpha - \{P(V - v_\alpha), P_\alpha\} = P_\alpha - \{P \sum_{\beta, \beta \neq \alpha} v_\beta, P_\alpha\}. \quad (7.8)$$

Furthermore, we have the well-known equation

$$P = P_0 - \{PV, P_0\}, \quad (7.9)$$

where P_0 is the principal solution of the multi-dimensional diffusion equation for the nonreacting particle system ($V=0$), and is given by, on the assumption of the medium of infinite volume,

$$\begin{aligned} P_0(X, Y; t | X_0, Y_0; t_0) &= \{4\pi D_A(t-t_0)\}^{-3N/2} \{4\pi D_B(t-t_0)\}^{-3M/2} \\ &\times \exp\left[-\sum_{i=1}^N |x_i - x_{i0}|^2 / 4D_A(t-t_0)\right] \\ &\times \exp\left[-\sum_{j=1}^M |y_j - y_{j0}|^2 / 4D_B(t-t_0)\right]. \end{aligned} \quad (7.10)$$

Then, of course one also has

$$P_\alpha = P_0 - \{P_\alpha v_\alpha, P_0\}. \quad (7.11)$$

Starting from these equations (7.8), (7.9) and (7.11), we can find a successive approximation which results in the binary collision expansion

$$\begin{aligned} P &= P_0 + \sum_\alpha u_\alpha - \sum_{\beta \neq \alpha} \{P_\beta v_\beta, u_\alpha\} + \sum_{\beta \neq \alpha, \gamma \neq \beta} \{P_\gamma v_\gamma, \{P_\beta v_\beta, u_\alpha\}\} \\ &\quad - \dots, \end{aligned} \quad (7.12)$$

where

$$u_\alpha = P_\alpha - P_0 = -\{P_\alpha v_\alpha, P_0\}, \quad (7.13)$$

and the symbols $\sum_{\alpha \neq \beta}$, $\sum_{\alpha \neq \beta, \gamma \neq \beta}$, etc., are the summation over all indices, excluding the values $\alpha \neq \beta$, $\gamma \neq \beta$.

The pair distribution function defined by

$$p(x_\alpha, y_\alpha; t | x_{\alpha 0}, y_{\alpha 0}; 0) = \int P_\alpha(X, Y; t | X_0, Y_0; 0) d\underline{X} d\underline{Y}, \quad (7.14)$$

where \underline{X} and \underline{Y} denote all the coordinates X and Y except for those of the pair α , i. e. x_α and y_α , satisfies the equation

$$\begin{aligned} \frac{\partial}{\partial t} p(x_\alpha, y_\alpha; t | x_{\alpha 0}, y_{\alpha 0}; 0) &= \{D_A \nabla_{x_\alpha}^2 + D_B \nabla_{y_\alpha}^2 - v_\alpha(x_\alpha, y_\alpha)\} \\ &\times p(x_\alpha, y_\alpha; t | x_{\alpha 0}, y_{\alpha 0}; 0). \end{aligned} \quad (7.15)$$

If we introduce new variables \mathbf{r} and \mathbf{z} defined by

$$\begin{aligned} \mathbf{r} &= x_\alpha - y_\alpha, \\ \mathbf{z} &= (D_B x_\alpha + D_A y_\alpha) / (D_A + D_B), \end{aligned} \quad (7.16)^*)$$

*) Here the bold-faced letters are used for convenience, but it should be noticed that x_α and y_α are also vectors.

and assume that v_α depends only on the relative coordinate \mathbf{r} , we can obtain the solution of Eq. (7.15) in the form

$$p = g(\mathbf{z}, \mathbf{z}_0; t) \rho(\mathbf{r}, \mathbf{r}_0; t), \quad (7.17)$$

where g and ρ are the solutions of the following equations:

$$\frac{\partial}{\partial t} g = \frac{D_A D_B}{D_A + D_B} \nabla_{\mathbf{z}}^2 g, \quad (7.18)$$

$$\frac{\partial}{\partial t} \rho = \{(D_A + D_B) \nabla_{\mathbf{r}}^2 - v_\alpha(\mathbf{r})\} \rho. \quad (7.19)$$

§ 8. Approximate calculation

Now we have to calculate the integral of Eq. (3.2), using the binary collision expansion (7.12), where $P(X, Y; t | X_0, Y_0; 0)$ is the solution of Eq. (6.1) for $N-k$ A particles and $M-k$ B particles. In our approximation we assume the uniform initial distribution, so that $f(X_0, Y_0)$ is given by $(1/V)^{N+M-2k}$.

The first term of expansion (7.12) obviously gives

$$(1/V)^{N+M-2k} \int P_0(X, Y; t | X_0, Y_0; 0) dX_0 dY_0 dX dY = 1, \quad (8.1)$$

because P_0 is the solution of unperturbed diffusion equation.

It is readily seen that the multiple integral

$$(1/V)^{N+M-2k} \int P_\alpha dX_0 dY_0 dX dY$$

can directly be performed for all coordinates except for those of the α pair, so that we have

$$(1/V)^{N+M-2k} \int u_\alpha dX_0 dY_0 dX dY = w(t) - 1, \quad (8.2)$$

$$w(t) = (1/V)^2 \int p(x_\alpha, y_\alpha; t | x_{\alpha 0}, y_{\alpha 0}; 0) dx_{\alpha 0} dy_{\alpha 0} dx_\alpha dy_\alpha, \quad (8.3)$$

where we have used Eq. (7.14). This can also be written as

$$w(t) = (1/V)^2 \int g(\mathbf{z}, \mathbf{z}_0; t) \rho(\mathbf{r}, \mathbf{r}_0; t) d\mathbf{z} d\mathbf{z}_0 d\mathbf{r} d\mathbf{r}_0.$$

If we can neglect the boundary effects, the integrals with respect to \mathbf{z} and \mathbf{z}_0 can directly be performed and they give simply a factor V , because g is the solution of the free diffusion equation (7.18). Therefore, under this assumption, we have

$$w(t) = (1/V) \int \rho(\mathbf{r}, \mathbf{r}_0; t) d\mathbf{r} d\mathbf{r}_0. \quad (8.4)$$

Thus all the $(N-k)(M-k)$ terms of the sum in the second term of Eq. (7.12)

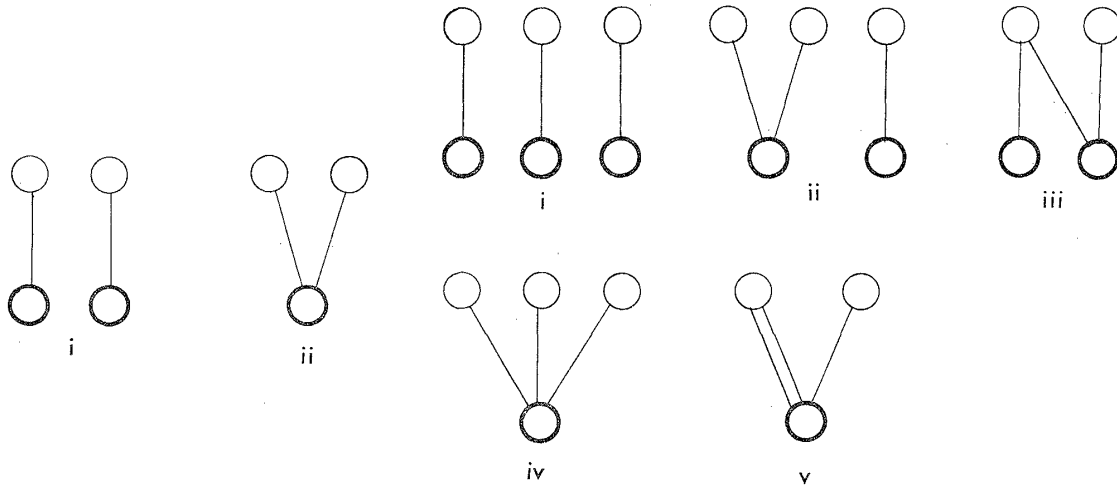


Fig. 1.

Fig. 2.

give the same integral (8.2).

Now let us consider the third term of Eq. (7.12). The integrals of the type

$$(1/V)^{N+M-2k} \int \{P_\beta v_\beta, u_\alpha\} dX_0 dY_0 dX dY \quad (8.5)$$

are divided into two cases. When the pairs α and β have no common particle, that is, the case i in Fig. 1, it is easily seen that the integral (8.5) can be reduced to

$$\begin{aligned} (1/V)^4 & \int_0^t dt' \int dx_{\alpha 0} dy_{\alpha 0} dx_{\alpha'} dy_{\alpha'} dx_{\beta'} dy_{\beta'} dx_{\beta} dy_{\beta} \\ & \times p(x_\beta, y_\beta; t | x_{\beta'}, y_{\beta'}; t') v(x_{\beta'}, y_{\beta'}) u(x_{\alpha'}, y_{\alpha'}; t' | x_{\alpha 0}, y_{\alpha 0}; 0) \\ & = \int_0^t \theta(t-t') \{v(t') - 1\} dt', \end{aligned} \quad (8.6)$$

where

$$\theta(t-t') = (1/V)^2 \int dx_\beta dy_\beta dx_{\beta'} dy_{\beta'} v(x_{\beta'}, y_{\beta'}) p(x_\beta, y_\beta; t | x_{\beta'}, y_{\beta'}; t'). \quad (8.7)$$

The number of terms which belong to the case i is $(N-k)(M-k)(N-k-1) \times (M-k-1)$ and they give the same contribution (8.6).

Next we shall consider the case that the pairs α and β have a common A particle whose coordinate is denoted by $x_{\alpha\beta}$. In this case, the integral is reduced to

$$\begin{aligned}
(1/V)^3 \int_0^t dt' \int dx_{\alpha\beta 0} dy_{\alpha 0} dx'_{x\beta} dy'_{\alpha} dy'_{\beta} dx_{\alpha\beta} dy_{\beta} \\
\times p(x_{\alpha\beta}, y_{\beta}; t | x'_{x\beta}, y'_{\beta}; t') v(x'_{x\beta}, y'_{\beta}) \\
\times u(x'_{x\beta}, y'_{\alpha}; t' | x_{\alpha\beta 0}, y_{\alpha 0}; 0). \quad (8.8)
\end{aligned}$$

It can be seen that, for the arguments of u , if we use the variables $\mathbf{r}_{\alpha 0}$, \mathbf{r}_{α}' , $z_{\alpha 0}$ and z_{α}' defined by (7.16) and neglect the boundary effects, the integration with respect to $z_{\alpha 0}$ can be readily performed; then it becomes independent of z_{α}' , so that the integration with respect to y_{α}' gives again the factor $w(t') - 1$. Then the remainder of the integral (8.8) has the same form as (8.7), so that (8.8) gives the same contribution as Eq. (8.6). It is easily seen that when the common particle is a B particle, the same result is obtained. The number of terms of the case ii is given by $(N-k)(M-k)\{(N-k-1) + (M-k-1)\}$; therefore summing up all the terms of these integrals, we obtain the contribution from the third term of Eq. (7.12):

$$(N-k)(M-k)\{(N-k)(M-k) - 1\} \int_0^t \theta(t-t') \{w(t') - 1\} dt'. \quad (8.9)$$

The integrals of the fourth and higher order terms of Eq. (7.12) contain many complicated multiple integrals which cannot be so simply factorized as we have done for the third term. For example, we shall consider the fourth term of Eq. (7.12), that is

$$\sum_{\alpha \neq \beta, \beta \neq \gamma} (1/V)^{N+M-2k} \int \{p_{\gamma} v_{\gamma}, \{p_{\beta} v_{\beta}, u_{\alpha}\}\} dX_0 dY_0 dX dY. \quad (8.10)$$

Various types of these multiple integrals are schematically shown in Fig. 2. It looks as if the integrals of diagrams of types ii, iii and iv can be factorized as well as type i, but it is not so and because of the time correlations, some of the diagrams of types ii and iii, depending on the order of bond indices α , β and γ , cannot be simply factorized. However, as an approximation, if we attribute the same contribution as that of diagram i to all these diagrams, we obtain

$$H(k) \{H(k) - 1\}^2 \int_0^t dt' \int_0^{t'} dt'' \theta(t-t') \theta(t'-t'') \{w(t'') - 1\}, \quad (8.11)$$

as the contribution from the fourth term of our expansion, where

$$H(k) = (N-k)(M-k). \quad (8.12)$$

Thus if we use the same approximation for the higher order terms, we may obtain

$$W_{N-k, N-k}(t) = 1 + H(k) \{w(t) - 1\} - H(k) \{H(k) - 1\} \int_0^t dt' \theta(t-t')$$

$$\begin{aligned} & \times \{w(t') - 1\} + H(k) \{H(k) - 1\}^2 \int_0^t dt' \int_0^{t'} dt'' \theta(t - t') \\ & \times \theta(t' - t'') \{w(t'') - 1\} - \dots \dots \dots \end{aligned} \quad (8.13)$$

Here, if we take into account the relation which corresponds to Eq. (3.6):

$$L(1-w; s) = \frac{1}{s} L(\theta; s), \quad (8.14)$$

the Laplace transform of Eq. (8.13) is given by

$$\begin{aligned} L(W_{N-k, N-k}; s) &= \frac{1}{s} [1 - H(k) L(\theta; s) + H(k) \{H(k) - 1\} L(\theta; s)^2 \\ &\quad - H(k) \{H(k) - 1\}^2 L(\theta; s)^3 + \dots] \\ &= \frac{1}{s} [1 - H(k) \sum_{i=0}^{\infty} (-1)^i \{H(k) - 1\}^i L(\theta; s)^{i+1}]. \end{aligned} \quad (8.15)$$

Thus if we know the solution of the two-body problem, we can calculate Eq. (8.15), then from our general formula (3.7) or (3.10) we can obtain the final result. However, the approximation adopted in the derivation of Eq. (8.15) is very crude and in order to have more precise information on the correlations of our many-body system, we need to calculate various terms appearing in the binary collision expansion in a more exact way.

§ 9. Diffusion controlled reaction rates

Finally, in this section we shall present an explicit result for the simplest case of diffusion controlled reactions. As we stated in the Introduction, the equation for two-body problems (7.19) have been investigated by many authors. In many of these investigations, reactions are taken into account by specifying the boundary conditions at the reaction radius $|\mathbf{r}| = R$, instead of the absorbing probability $v(\mathbf{r})$. Two kinds of boundary conditions are considered. In the "Smoluchowski boundary condition", it is assumed that two molecules react immediately upon collision; thus $\rho(r)$ must be zero at $|\mathbf{r}| = R$. Collins and Kimball⁵⁾ examined the case that the rate of reaction on the sphere of radius R is proportional to the flux of counter particles through that surface, which is usually called the "radiation boundary condition".

In these cases, it was shown that the stationary reaction rate is given by $4\pi D_{AB} R^* / V$, where $D_{AB} = D_A + D_B$ and R^* is the effective reaction radius. It seems to us that there may be some ambiguous points in the direct application of this result to our formula, because it should be noticed that this stationary diffusion controlled reaction rate is obtained for an essentially infinite system, assuming the constant probability density of the counter particles at infinite distance. However, if we can assume that this stationary rate is valid for short

time ranges for the finite system, we may be able to use this result as the solution of our two-body problem. Then we have

$$w(t) = \exp(-4\pi D_{AB}R^*t/V), \quad (9.1)$$

and calculating (8.14) we obtain

$$L(\theta; s) = \frac{4\pi D_{AB}R^*/V}{s + 4\pi D_{AB}R^*/V}. \quad (9.2)$$

Equation (8.15) can be written in the form

$$L(W_{N-k, N-k}; s) = \frac{1}{s} \frac{1 - L(\theta; s)}{1 + \{H(k) - 1\} L(\theta; s)}. \quad (9.3)$$

Hence, using Eq. (9.2) we have

$$L(W_{N-k, N-k}; s) = \frac{1}{s + 4\pi D_{AB}R^*H(k)/V}. \quad (9.4)$$

The inverse transformation of Eq. (9.4) becomes

$$W_{N-k, N-k}(t) = \exp[-4\pi D_{AB}R^*H(k)t/V]. \quad (9.5)$$

Thus, in this case, from Eq. (4.2) the rate function is given by

$$K_{N-k} = 4\pi D_{AB}R^*H(k)/V = \frac{4\pi D_{AB}R^*}{V} (N-k)(M-k). \quad (9.6)$$

§ 10. Summary

In this paper we have developed a systematic formulation of bimolecular reaction processes in liquids as a many-body problem. Space-time correlations, which are completely taken into account in the general formula (2.3), have been partially smoothed out by reducing the problem to that of Markov process; this seems to be allowed only when the uniform distribution is assumed for the initial ensemble.

In particular when the rate function defined by Eq. (4.2) is independent of time, the process becomes a rather simple stationary Markov process, which is essentially a random walk problem and is described by a differential difference equation (4.4) or (4.5). Moreover it has been shown that the solution of these equations in the first order approximation gives just the law of mass action. In more general cases which can be described by Eq. (3.11), in order to have that equation in an explicit form, the multi-dimensional diffusion equation with pair absorbing interactions must be solved. This equation will be calculated using various techniques developed in the theory of many-body problems. Here we have adopted the binary collision expansion method and have showed that in a simple approximation, we can have the well-known result obtained previously for the diffusion controlled bimolecular reactions.

In fact what we have discussed here is only that if we start from the general description of the time development of our many-body system, the results of the usual simple phenomenological equations can be derived through many steps of the approximations. However, various formulae developed here will give the ways of investigating more detailed effects of the space time correlations and then deviations from simple laws of the usual theories of chemical kinetics. These problems will be discussed in the near future.

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Appendix I

By applying the Laplace transformation to Eq. (4.4), that is

$$\frac{d}{dt} W_{N-n,N} = \kappa(N-n+1)(M-n+1)W_{N-n+1,N} - \kappa(N-n)(M-n)W_{N-n,N}, \quad (\text{I.1})$$

we obtain

$$L(W_{N-n,N}; s) = \frac{\kappa H(n-1)}{s + \kappa H(n)} L(W_{N-n+1,N}; s), \text{ for } n \geq 1, \quad (\text{I.2})$$

where $H(n) = (N-n)(M-n)$. For $n=0$, we have

$$\frac{d}{dt} W_{N,N} = -\kappa N M W_{N,N} \quad (\text{I.3})$$

with the initial condition $W_{N,N}(0) = 1$; hence

$$W_{N,N}(t) = \exp(-\kappa N M t), \quad L(W_{N,N}; s) = \frac{1}{s + \kappa N M}. \quad (\text{I.4})$$

Using Eqs. (I.2) and (I.3), we obtain by iteration

$$L(W_{N-n,N}; s) = \frac{\kappa^n \prod_{k=1}^n H(k-1)}{\prod_{k=0}^n [s + \kappa H(k)]}. \quad (\text{I.5})$$

Now, if we employ the partial-fraction representation, we get

$$L(W_{N-n,N}; s) = \sum_{k=0}^n \frac{\lambda_{nk}}{s + \kappa H(k)}, \quad (\text{I.6})$$

where

$$\lambda_{nk} = [H(0)H(1)\cdots H(n-1)] \{[H(0)-H(k)][H(1)-H(k)]\cdots [H(k-1)-H(k)][H(k+1)-H(k)]\cdots [H(n)-H(k)]\}^{-1}.$$

Hence

$$L(W_{N-n,N}; s) = \prod_{l=1}^n H(l-1) \sum_{k=0}^n \{[s + \kappa H(k)] \prod_{\substack{0 \leq l \leq n \\ k \neq l}} [H(l) - H(k)]\}^{-1}. \quad (\text{I.7})$$

The inverse transformation of Eq. (I.7) gives the final expression for the solution of Eq. (4.4):

$$W_{N-n,N}(t) = \sum_{k=0}^n e^{-\kappa H(k)t} \left\{ \prod_{l=1}^n H(l-1) / \prod_{\substack{0 \leq l \leq n \\ l \neq k}} [H(l) - H(k)] \right\}. \quad (\text{I.8})$$

Here we shall compare this result with our general formula developed in § 3. If we assume the stationary condition (4.3), from Eq. (4.2) we obtain

$$W_{N-k,N-k}(t) = e^{-\kappa H(k)t}. \quad (\text{I.9})$$

Hence, we have

$$L(1 - W_{N-k,N-k}; s) = \frac{\kappa H(k)}{s[s + \kappa H(k)]} \quad (\text{I.10})$$

and

$$L(W_{N-n,N-n}; s) = \frac{1}{s + \kappa H(n)}. \quad (\text{I.11})$$

Thus it can be seen that, in this case, the solution (I.5) is derived directly from the general formula (3.7) as a special case.

When $M \gg N$, it can be easily shown that Eq. (I.8) becomes a Bernoulli distribution, that is, if we use the approximation $H(l) = M(N-l)$, we obtain

$$\begin{aligned} W_{N-n,N}(t) &= \sum_{k=0}^n e^{-\kappa M(N-k)t} \left\{ \frac{N!}{(N-n)!} \frac{1}{(-1)^{n-k} (n-k)! k!} \right\} \\ &= \frac{N!}{(N-n)! n!} e^{-\kappa M N t} \sum_{k=0}^n \frac{n!}{(n-k)! k!} (-1)^{n-k} e^{\kappa M k t} \\ &= \frac{N!}{(N-n)! n!} e^{-\kappa M N t} [e^{\kappa M t} - 1]^n \\ &= \frac{N!}{(N-n)! n!} p^{N-n} q^n, \end{aligned}$$

where

$$p = e^{-\kappa M t}, \quad q = 1 - e^{-\kappa M t}.$$

Thus, if we use the variable $m = N - n$, we have

$$W_m(t) = \frac{N!}{(N-m)!m!} p^m q^{N-m}. \quad (\text{I} \cdot 12)$$

The mean and the mean square deviation of the Bernoulli distribution (I·12) is given by

$$\langle m \rangle = Np = Ne^{-\kappa M t}, \quad (\text{I} \cdot 13)$$

$$\sigma^2(t) = \langle (m - \langle m \rangle)^2 \rangle = Npq = Ne^{-\kappa M t} (1 - e^{-\kappa M t}), \quad (\text{I} \cdot 14)$$

which agree with the results (4·11) and (5·8) obtained by solving the differential equations for the moments on the assumption of the relation (5·3).

Furthermore, owing to the DeMoivre-Laplace limit theorem, asymptotic formula of Eq. (I·12) is given by¹⁶⁾

$$W_m(t) = (2\pi Npq)^{-1/2} e^{-(m-Np)^2/2Npq} \quad (\text{I} \cdot 15)$$

under the condition $N \gg m \gg 1$. This result may suggest the plausibility of our assumption used in § 5.

Appendix II

—Reversible bimolecular reactions—

Though we have restricted our attention to irreversible reactions in the text, it will be shown that the similar formulation can be derived for a more general case in which the inverse reaction $AB \rightarrow A + B$ exists.

We consider a system in which N particles of type A and M particles of type B are initially distributed by medium of volume V . In order to formulate the reaction process, let us introduce the following probability functions: $Z_n(t)$ is the probability that one reaction of association or dissociation of an AB pair occurs between t and $t + dt$ and the number of AB complexes becomes n during that time interval, $T_{n,n-1}(t)$ is the probability of the first association defined in the text where we have denoted it by $T_{N-n,N-n+1}$, and $R_{n,n+1}(t)$ is the probability of the first dissociation defined in just the same way as $T_{n,n-1}$.

Then the probability that at time t n AB complexes are found, which is denoted by $W_{N-n,N}(t)$ in the text, can be written as

$$W_{N-n,N}(t) = \int_0^t U_{N-n,N-n}(t-t') Z_n(t') dt', \quad (\text{II} \cdot 1)$$

where $U_{N-n,N-n}(t)$ is the probability that $N-n$ A particles and $M-n$ B particles with uniform initial distribution remain unreacted until time t . In the irreversible case, it was unnecessary to distinguish this probability from $W_{N-n,N-n}(t)$, because the reaction process always proceeds to one direction. From the definitions there exists a relation

$$U_{N-n, N-n}(t) + \int_0^t [T_{n+1, n}(t') + R_{n-1, n}(t')] dt' = 1, \quad (\text{II} \cdot 2)$$

and also we have

$$Z_n(t) = \int_0^t T_{n, n-1}(t-t') Z_{n-1}(t') dt' + \int_0^t R_{n, n+1}(t-t') Z_{n+1}(t') dt'. \quad (\text{II} \cdot 3)$$

Hence, by the Laplace transformation, we obtain

$$Z_n(s) = T_{n, n-1}(s) Z_{n-1}(s) + R_{n, n+1}(s) Z_{n+1}(s), \quad (\text{II} \cdot 4)$$

where we have used the simple notation for the Laplace transforms by putting argument s . Equation (II.4) can also be written in the form

$$Z_{n+1}(s) = \frac{1}{R_{n, n+1}(s)} Z_n(s) - \frac{T_{n, n-1}(s)}{R_{n, n+1}(s)} Z_{n-1}(s). \quad (\text{II} \cdot 5)$$

Now if we introduce the vectors and matrices defined by

$$\mathbf{Z}_n(s) = \begin{pmatrix} Z_n(s) \\ Z_{n-1}(s) \end{pmatrix}, \quad \mathbf{T}_n(s) = \begin{pmatrix} \frac{1}{R_{n, n+1}(s)} & -\frac{T_{n, n-1}(s)}{R_{n, n+1}(s)} \\ 1 & 0 \end{pmatrix}, \quad (\text{II} \cdot 6)$$

we obtain, by successive applications of Eq. (II.5),

$$\mathbf{Z}_{n+1}(s) = \mathbf{T}_n \mathbf{Z}_n = \prod_{i=0}^n \mathbf{T}_i \mathbf{Z}_0, \quad (\text{II} \cdot 7)$$

where

$$\mathbf{T}_0 = \begin{pmatrix} \frac{1}{R_{0,1}(s)} & 0 \\ 1 & 0 \end{pmatrix}, \quad \mathbf{Z}_0(s) = \begin{pmatrix} Z_0(s) \\ 0 \end{pmatrix}. \quad (\text{II} \cdot 8)$$

Hence, by Eq. (II.1) we have

$$W_{N-n, N}(s) = U_{N-n, N-n} \mathbf{u}^* \prod_{i=0}^{n-1} \mathbf{T}_i \mathbf{u} Z_0(s), \quad (\text{II} \cdot 9)$$

where

$$\mathbf{u} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \mathbf{u}^* = (1 \ 0). \quad (\text{II} \cdot 10)$$

In Eq. (II.9), $U_{N-n, N-n}$ and \mathbf{T}_i 's are expressed in terms of probabilities of the first reaction $R_{n-1, n}$ and $T_{n+1, n}$ by Eqs. (II.2) and (II.6), on the other hand $Z_0(s)$ can be obtained by the normalization condition

$$\sum_{n=0}^N W_{N-n,N}(t) = 1, \quad (\text{II} \cdot 11)$$

that is,

$$\sum_{n=0}^N W_{N-n,N}(s) = 1/s. \quad (\text{II} \cdot 12)$$

Thus we have the formula

$$W_{N-n,N}(s) = \frac{1}{s} \frac{U_{N-n,N-n} \mathbf{u}^* \prod_{i=0}^{n-1} \mathbf{T}_i \mathbf{u}}{\sum_{n=0}^N U_{N-n,N-n} \mathbf{u}^* \prod_{i=0}^{n-1} \mathbf{T}_i \mathbf{u}}. \quad (\text{II} \cdot 13)$$

Now, as a special case, we shall consider the stationary reaction rate, that is, we assume probabilities of the first reaction $T_{n,n-1}$ and $R_{n,n+1}$ to be given in the forms

$$\begin{aligned} T_{n,n-1} &= \kappa H(n-1) U_{N-n+1,N-n+1}, \\ R_{n,n+1} &= \mu(n+1) U_{N-n-1,N-n-1}, \end{aligned} \quad (\text{II} \cdot 14)$$

where $H(n) = (N-n)(M-n)$. Then using Eqs. (II.1) and (II.4), we get

$$Z_n(t) = \kappa H(n-1) W_{N-n+1,N}(t) + \mu(n+1) W_{N-n-1,N}(t). \quad (\text{II} \cdot 15)$$

Differentiating Eq. (II.1) and using the expression

$$\frac{d}{dt} \log U_{N-n,N-n} = -\kappa H(n) - \mu n, \quad (\text{II} \cdot 16)$$

which can be derived from Eqs. (II.2) and (II.14), we obtain

$$\begin{aligned} \frac{d}{dt} W_{N-n,N}(t) &= \kappa H(n-1) W_{N-n+1,N}(t) + \mu(n+1) W_{N-n-1,N}(t) \\ &\quad - \{\kappa H(n) + \mu n\} W_{N-n,N}(t). \end{aligned} \quad (\text{II} \cdot 17)$$

This is the stochastic equation which describes the reversible bimolecular reaction processes.

By Eq. (II.13) the Laplace transform of the solution of this case is given by

$$W_{N-n,N}(s) = \frac{1}{s} \frac{\frac{1}{s+H(n)+n} \mathbf{u}^* \prod_{i=0}^{n-1} \mathbf{T}_i(s) \mathbf{u}}{\sum_{n=0}^N \frac{1}{s+H(n)+n} \mathbf{u}^* \prod_{i=0}^{n-1} \mathbf{T}_i(s) \mathbf{u}}, \quad (\text{II} \cdot 18)$$

where

$$\begin{aligned} \mathbf{T}_i(s) &= \begin{pmatrix} \frac{s+\kappa H(i+1)+\mu(i+1)}{\mu(i+1)} & -\frac{\kappa H(n-1)[s+\kappa H(n+1)+\mu(n+1)]}{\mu(n+1)[s+\kappa H(n-1)+\mu(n-1)]} \\ 1 & 0 \end{pmatrix} \\ &\quad \text{for } i \geq 1, \end{aligned} \quad (\text{II} \cdot 19)$$

$$\mathbf{T}_0(s) = \begin{pmatrix} s + \kappa H(1) + \mu & 0 \\ \mu & 0 \\ 1 & 0 \end{pmatrix}.$$

Finally, in just the same manner as we have done in § 5, it can be easily shown that, in the first order approximation, Eq. (II·17) leads to the law of mass action

$$\frac{d}{dt} C_A = -\nu C_A C_B + \mu C_{AB}. \quad (\text{II} \cdot 20)$$

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