Stochastic Formulation of Entropy Production due to Second-Order Reaction

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Entropy production, originated from an ideal gas second-order reaction taking place in a closed system, has been stochastically formulated by defining the entropy in a form similar to the conditional entropy used in the theory of information. The entropy is introduced in the natural way as a result of the partial factorization of joint probability for reaction states devised for the approximate solution of the stochastic process of the second-order reaction. The entropy production has also been discussed in comparison with the usual one.

The stochastic nonequilibrium thermodynamics of reaction systems can be studied by the correlation of probability to entropy on the proposition that chemical reaction is a random process. The author has stochastically discussed the nonequilibrium thermodynamics for first-order reactions in closed and open systems.[1] It has been assumed that the entropy change $\varDelta_i S$ due to a chemical reaction is of Gibbsian type, *viz.*,

$$\varDelta_i S = -\boldsymbol{k}\sum_{\boldsymbol{n}} P(\boldsymbol{n};\ t)\ln[P(\boldsymbol{n};\ t)/P(\boldsymbol{n};\ \infty)] \tag{1}$$

or

$$S = -\boldsymbol{k}\langle\ln[P(\boldsymbol{n};\ t)/P(\boldsymbol{n};\ \infty)]\rangle + S_e, \tag{1'}$$

where $\boldsymbol{k}$ is Boltzmann's constant, $P(\boldsymbol{n};\ \mathrm{t})$ the probability distribution for the set $\boldsymbol{n}=\{n_\gamma\}$ of all the numbers of molecules of reacting species γ's at time t, $P(\boldsymbol{n};\ \infty)$ the corresponding equilibrium probability distribution, $\varDelta_i S=S-S_e$ (S_e is the entropy for the equilibrium probability distribution) and the angular brackets denote the average over all possible reaction states.

As an example, we consider the reaction A⇆B. The probability distribution for reaction states is given by the binomial distribution $P(\boldsymbol{n};\ t)=(n!/\prod_\gamma n_\gamma!)\prod_\gamma\{p_\gamma(t)\}^{n_\gamma}$, in which $n=\sum_\gamma n_\gamma$ (γ=A, B) is the total number of molecules and $p_\gamma(t)$ the probability for a molecule of reacting species γ to be found in the reaction system. According to Eq. (1), the entropy change can be written as

$$\begin{aligned}\varDelta_i S &= -\boldsymbol{k}\sum_\gamma\langle n_\gamma\rangle\ln[p_\gamma(t)/q_\gamma]\\ &= -\boldsymbol{k}\sum_\gamma\langle n_\gamma\rangle\ln[\langle n_\gamma\rangle/\langle n_\gamma\rangle_e],\end{aligned} \tag{2}$$

where q_γ is the probability corresponding to $p_\gamma(t)$ in equilibrium state. This is identified with the result from the usual nonequilibrium thermodynamics, in which the hypothesis of local equilibrium[2] plays an important role. It should be stressed, here, that the hypothesis of local equilibrium is also implicitly involved in Eq. (1), since the equilibrium probability distribution $P(\boldsymbol{n};\ \infty)$ is assumed to be retained throughout the reaction time.

For the system in which a second-order reaction occurs, however, the stochastic formulation of nonequilibrium thermodynamics remains unsettled. This may well be due to the difficulty in finding the probability distribution to facilitate the evaluation of stochastic entropy. When the probability distribution, even though it is approximate, is found at all, the entropy change can be calculated by Eq. (1). The plan of this paper is as follows. We describe a second-order reaction by the stochastic process linearized with the transition probability variable with time on the assumption of the partial factorization of the joint probability distribution for reaction states, and at the same time we define the stochastic entropy in a form similar to the conditional entropy in the theory of information.[3]

Stochastic Model for Second-Order Reaction

For the sake of simplicity, we consider a second-order reaction in ideal gases

$$\mathrm{A} + \mathrm{B} \rightleftarrows \mathrm{C}. \tag{I}$$

Letting the random variables $X_\mathrm{A}(t)$, $X_\mathrm{B}(t)$, and $X_\mathrm{C}(t)$ represent the numbers of molecules of reacting species A, B, and C at time t, respectively, the stochastic process is then described by the differential-difference equation,

$$\begin{aligned}&\frac{\mathrm{d}}{\mathrm{d}t}P(n_\mathrm{A},\ n_\mathrm{B},\ n_\mathrm{C};\ t)\\ &\quad= \lambda(n_\mathrm{A}+1)(n_\mathrm{B}+1)P(n_\mathrm{A}+1,\ n_\mathrm{B}+1,\ n_\mathrm{C}-1;\ t)\\ &\quad\quad- (\lambda n_\mathrm{A}n_\mathrm{B}+\lambda' n_\mathrm{C})P(n_\mathrm{A},\ n_\mathrm{B},\ n_\mathrm{C};\ t)\\ &\quad\quad+ \lambda'(n_\mathrm{C}+1)P(n_\mathrm{A}-1,\ n_\mathrm{B}-1,\ n_\mathrm{C}+1;\ t)\end{aligned} \tag{3}$$

where $P(n_\mathrm{A},\ n_\mathrm{B},\ n_\mathrm{C};\ t)=\mathrm{Prob.}\{X_\mathrm{A}(t)=n_\mathrm{A},\ X_\mathrm{B}(t)=n_\mathrm{B},\ X_\mathrm{C}(t)=n_\mathrm{C}\}$ denotes the joint probability that there are n_A, n_B, and n_C molecules of reacting species A, B, and C in the reaction system at time t, respectively, and λ and λ' are the rate constants defined on the assumption that the transition probabilities of reaction processes of A+B→C and A+B←C in the time interval $(t,\ t+\mathrm{d}t)$ are given by $\lambda\ n_\mathrm{A}n_\mathrm{B}\mathrm{d}t$ and $\lambda' n_\mathrm{C}\mathrm{d}t$, respectively.

It is a complicated problem, soluble in principle, to find the probability distribution $P(n_\mathrm{A},\ n_\mathrm{B},\ n_\mathrm{C};\ t)$ from Eq. (3), which is nonlinear with respect to the numbers of molecules. In order to obtain its approximate solution, however, we attempt to reform Eq. (3) into the linear equation of only the number of molecules of reacting species C, n_C. If the reaction system is in the thermodynamic limit such that the total number of molecules taking part in reaction is sufficiently large,

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

2) S. R. de Groot and P. Mazur, "Non-Equilibrium Thermodynamics," North-Holland Publishing Co., Amsterdam (1962), p. 23.

3) A. I. Khinchin, "Mathematical Foundations of Information Theory," Dover Publications Inc., New York (1957), p. 35.

it is possible to assume the partial factorization of the joint probability[4]

$$P(n_A,\ n_B,\ n_C;\ t) = P(n_A;\ t)P(n_B,\ n_C;\ t) \tag{4, A}$$

or

$$P(n_A,\ n_B,\ n_C;\ t) = P(n_B;\ t)P(n_A,\ n_C;\ t). \tag{4, B}$$

Such a factorization, as will be shown later, is made to preserve at least the stochastic process of the reaction. Applying the factorization (4, A) to Eq. (3) and taking the summation over all possible values of random variable $X_A(t)$, we obtain

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}&P(n_B,\ n_C;\ t)\\ &= \lambda\langle n_A\rangle(n_B+1)P(n_B+1,\ n_C-1;\ t)\\ &\quad - (\lambda\langle n_A\rangle n_B+\lambda' n_C)P(n_B,\ n_C;\ t)\\ &\quad + \lambda'(n_C+1)P(n_B-1,\ n_C+1;\ t).\end{aligned} \tag{5}$$

From Eq. (5), we can easily derive the rate equation with respect to the mean $\langle n_C\rangle$,

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle n_C\rangle = \lambda\langle n_A\rangle\langle n_B\rangle-\lambda'\langle n_C\rangle. \tag{6}$$

This is of the uncorrelated form of the alternative rate equation derived directly from Eq. (3),

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle n_C\rangle = \lambda\langle n_A n_B\rangle-\lambda'\langle n_C\rangle, \tag{7}$$

which, in the thermodynamic limit, is practically equivalent to Eq. (6). If the initial numbers of molecules of reacting species A and B are denoted by $n_A{}^{(0)}$ and $n_B{}^{(0)}$, respectively, equation (6) is written as

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle n_C\rangle = \lambda(n_A{}^{(0)}-\langle n_C\rangle)(n_B{}^{(0)}-\langle n_C\rangle)-\lambda'\langle n_C\rangle. \tag{6'}$$

Solving this differential equation, we obtain, in agreement with the deterministic theory,

$$\langle n_C\rangle = \frac{\alpha\beta(1-\exp[-\lambda(\alpha-\beta)t])}{\alpha-\beta\exp[-\lambda(\alpha-\beta)t]}, \tag{8}$$

where α and β are the roots of

$$\langle n_C\rangle^2 - (n_A{}^{(0)}+n_B{}^{(0)}+\lambda'/\lambda)\langle n_C\rangle + n_A{}^{(0)}n_B{}^{(0)} = 0. \tag{9}$$

Let us return to Eq. (5). If the transition probability variable with time is defined by

$$\lambda_A(t) = \lambda\langle n_A\rangle, \tag{10}$$

where

$$\langle n_A\rangle = n_A{}^{(0)} - \frac{\alpha\beta(1-\exp[-\lambda(\alpha-\beta)t])}{\alpha-\beta\exp[-\lambda(\alpha-\beta)t]}, \tag{11}$$

equation (5) becames

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}&P(n_B,\ n_C;\ t)\\ &= \lambda_A(t)(n_B+1)P(n_B+1,\ n_C-1;\ t)\\ &\quad - (\lambda_A(t)n_B+\lambda' n_C)P(n_B,\ n_C;\ t)\\ &\quad + \lambda'(n_C+1)P(n_B-1,\ n_C+1;\ t)\end{aligned} \tag{5'}$$

or

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}&P(n_C;\ t)\\ &= \lambda_A(t)\{n_B{}^{(0)}-(n_C-1)\}P(n_C-1;\ t)\\ &\quad - \{\lambda_A(t)(n_B{}^{(0)}-n_C)+\lambda' n_C\}P(n_C;\ t)\\ &\quad + \lambda'(n_C+1)P(n_C+1;\ t),\end{aligned} \tag{5''}$$

which is just the same because of Prob. $\{X_B(t)=n_B,\ X_C(t)=n_C\}=\text{Prob.}\{X_B(t)=n_B^{(0)}-n_C,\ X_C(t)=n_C\}=$ Prob. $\{X_C(t)=n_C\}$ on the basis of the introduction of the transition probability $\lambda_A(t)$.

To solve Eq. (5''), let us define the generating function

$$G(z_C;\ t) = \sum_{n_C} z_C{}^{n_C}P(n_C;\ t),\quad 0<|z_C|\leq 1. \tag{12}$$

From Eq. (5''), then, we obtain the partial differential equation

$$\frac{\partial G}{\partial t} = \{\lambda_A(t)+\lambda'\}(1-z_C)\frac{\partial G}{\partial z_C} - n_B{}^{(0)}\lambda_A(t)(1-z_C)G, \tag{13}$$

where the initial condition is given by $G(z_C;\ 0)=1$, which corresponds to the initial condition for Eq. (5''), $P(n_C;\ 0)=\delta_{n_C,0}$. After rather lengthy algebraic manipulations, it can be found that the solution of Eq. (13) is of the form

$$\begin{aligned}G(z_C;\ t) = \Bigg\{&\frac{\alpha-n_A{}^{(0)}-(\beta-n_A{}^{(0)})\exp[-\lambda(\alpha-\beta)t]}{\alpha-\beta\exp[-\lambda(\alpha-\beta)t]}\\ &+\frac{n_A{}^{(0)}(1-\exp[-\lambda(\alpha-\beta)t])}{\alpha-\beta\exp[-\lambda(\alpha-\beta)t]}z_C\Bigg\}^{n_B{}^{(0)}}.\end{aligned} \tag{14}$$

Performing the binomial expansion of the right-hand side of this equation, we have, according to Eq. (12),

$$\begin{aligned}P(n_C;\ t) = &\binom{n_B{}^{(0)}}{n_C}\left\{\frac{n_A{}^{(0)}(1-\exp[-\lambda(\alpha-\beta)t])}{\alpha-\beta\exp[-\lambda(\alpha-\beta)t]}\right\}^{n_C}\\ &\times\left\{\frac{\alpha-n_A{}^{(0)}-(\beta-n_A{}^{(0)})\exp[-\lambda(\alpha-\beta)t]}{\alpha-\beta\exp[-\lambda(\alpha-\beta)t]}\right\}^{n_B{}^{(0)}-n_C}.\end{aligned} \tag{15}$$

This is the probability distribution on the understanding that the reacting species A takes part in the reaction through the mean number of molecules, $\langle n_A\rangle$. Of course, from the probability distribution (15), we obtain the mean $\langle n_C\rangle$ consistent with Eq. (8).

Let us find the probability $P(n_A;\ t)$. For this purpose, we introduce again the generating function defined by

$$g(z_A;\ t) = \sum_{n_A} z_A{}^{n_A}\{\sum_{n_B,\ n_C} P(n_A,\ n_B,\ n_C;\ t)\}, \tag{16}$$

$$0<|z_A|\leq 1$$

which may be called a reduced one. Thus, we have from Eq. (3),

$$\frac{\partial g}{\partial t} = (1-z_A)\left\{\lambda\langle n_B\rangle\frac{\partial g}{\partial z_A}-\lambda'\langle n_C\rangle g\right\}, \tag{17}$$

where the factorization (4, A) has been taken into account. Since $\lambda'\langle n_C\rangle_e/\lambda\langle n_B\rangle_e=\langle n_A\rangle_e$ at equilibrium, we find straight from Eq. (17)

$$g(z_A\colon\ \infty) = \exp[(z_A-1)\langle n_A\rangle_e]. \tag{18}$$

This shows that the equilibrium probability distribution is Poissonian;

$$P(n_A;\ \infty) = \exp(-\langle n_A\rangle_e)\langle n_A\rangle_e{}^{n_A}/n_A!. \tag{19}$$

The time-dependent solution of Eq. (17) is of the same form as Eq. (18),

$$g(z_A;\ t) = \exp[(z_A-1)\langle n_A\rangle] \tag{20}$$

obtained by means of the initial condition, $g(z_A;\ 0)=\exp[(z_A-1)n_A{}^{(0)}]$, in which we have assumed

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[4] I. Oppenheim, K. E. Shuler, and G. H. Weiss, *J. Chem. Phys.*, **50**, 460 (1969).

$\langle n_{\mathrm{A}}\rangle_{\mathrm{initial}}=n_{\mathrm{A}}{}^{(0)}$. To this generating function corresponds the Poisson distribution,

$$P(n_{\mathrm{A}};\ t)=\exp(-\langle n_{\mathrm{A}}\rangle)\langle n_{\mathrm{A}}\rangle^{n_{\mathrm{A}}}/n_{\mathrm{A}}!, \tag{21}$$

where the mean $\langle n_{\mathrm{A}}\rangle$ is consistent with the value given by Eq. (11).

It should be mentioned that Eq. (5′) or (5″) describes the stochastic process of the modified second-order reaction as follows:

$$\mathrm{B}(\langle\mathrm{A}\rangle)\rightleftarrows\mathrm{C}, \tag{II, A}$$

where the symbol $\langle\mathrm{A}\rangle$ in parentheses indictes the hypothesis that the average change of the number of A molecules is incorporated beforehand in the transition probability $\lambda_{\mathrm{A}}(t)$ at an arbitrarily fixed time t. On the other hand, assuming the factorization (4, B), we may similarly consider the other modified second-order reaction

$$\mathrm{A}(\langle\mathrm{B}\rangle)\rightleftarrows\mathrm{C}. \tag{II, B}$$

Thus, we can symbolically express the probability for the required reaction (I), $\mathcal{P}(\mathrm{A}+\mathrm{B}\rightleftarrows\mathrm{C})$, by

$$\mathcal{P}(\mathrm{A}+\mathrm{B}\rightleftarrows\mathrm{C})=\mathcal{P}(\mathrm{A})\mathcal{P}(\mathrm{B}(\langle\mathrm{A}\rangle)\rightleftarrows\mathrm{C}) \tag{22, A}$$

or

$$\mathcal{P}(\mathrm{A}+\mathrm{B}\rightleftarrows\mathrm{C})=\mathcal{P}(\mathrm{B})\mathcal{P}(\mathrm{A}(\langle\mathrm{B}\rangle)\rightleftarrows\mathrm{C}). \tag{22, B}$$

In Eq. (22, A), the probability $\mathcal{P}(\mathrm{B}(\langle\mathrm{A}\rangle)\rightleftarrows\mathrm{C})$ for the modified reaction (II, A) may be regarded as a conditional probability, calculated on the assumption that the average change of the number of A molecules is realized beforehand with the probability $\mathcal{P}(\mathrm{A})$. Equation (22, A) or (22, B), together with the Gibbs entropy postulate (1) or (1′), forms the basis of the stochastic formulation of nonequilibrium thermodynamics of reaction (I).

Stochastic Entropy

Following the Gibbs entropy postulate (1′), we have, as the stochastic entropy for the probability $\mathcal{P}(\mathrm{A}+\mathrm{B}\rightleftarrows\mathrm{C})$,

$$\begin{aligned}S(\mathrm{A}+\mathrm{B}\rightleftarrows\mathrm{C})&=-\boldsymbol{k}\langle\ln[\mathcal{P}(\mathrm{A}+\mathrm{B}\rightleftarrows\mathrm{C})/\\&\quad\mathcal{P}_e(\mathrm{A}+\mathrm{B}\rightleftarrows\mathrm{C})]\rangle+S_e(\mathrm{A}+\mathrm{B}\rightleftarrows\mathrm{C}).\end{aligned} \tag{23}$$

As an example, if we apply the relation (22, A) to Eq. (23), we can write the stochastic entropy $S(\mathrm{A}+\mathrm{B}\rightleftarrows\mathrm{C})$ in the form

$$\begin{aligned}&S(\mathrm{A}+\mathrm{B}\rightleftarrows\mathrm{C})\\&=-\boldsymbol{k}\{\sum_{\mathrm{A}}\mathcal{P}(\mathrm{A})\ln[\mathcal{P}(\mathrm{A})/\mathcal{P}_e(\mathrm{A})]\sum_{\mathrm{C}}\mathcal{P}(\mathrm{B}(\langle\mathrm{A}\rangle)\rightleftarrows\mathrm{C})\\&\quad+\sum_{\mathrm{A}}\mathcal{P}(\mathrm{A})\sum_{\mathrm{C}}\mathcal{P}(\mathrm{B}(\langle\mathrm{A}\rangle)\rightleftarrows\mathrm{C})\ln[\mathcal{P}(\mathrm{B}(\langle\mathrm{A}\rangle)\rightleftarrows\mathrm{C})/\\&\quad\mathcal{P}_e(\mathrm{B}(\langle\mathrm{A}\rangle)\rightleftarrows\mathrm{C})]\}+S_e(\mathrm{A}+\mathrm{B}\rightleftarrows\mathrm{C}).\end{aligned} \tag{24}$$

However, owing to the normalizations $\sum_{\mathrm{A}}\mathcal{P}(\mathrm{A})=1$ and $\sum_{\mathrm{C}}\mathcal{P}(\mathrm{B}(\langle\mathrm{A}\rangle)\rightleftarrows\mathrm{C})=1$, this equation now becomes

$$\begin{aligned}&S(\mathrm{A}+\mathrm{B}\rightleftarrows\mathrm{C})\\&=-\boldsymbol{k}\{\langle\ln[\mathcal{P}(\mathrm{A})/\mathcal{P}_e(\mathrm{A})]\rangle\\&\quad+\langle\ln[\mathcal{P}(\mathrm{B}(\langle\mathrm{A}\rangle)\rightleftarrows\mathrm{C})/\mathcal{P}_e(\mathrm{B}(\langle\mathrm{A}\rangle)\rightleftarrows\mathrm{C})]\rangle\}\\&\quad+S_e(\mathrm{A}+\mathrm{B}\rightleftarrows\mathrm{C}).\end{aligned} \tag{25}$$

If we furthermore decompose the entropy $S_e(\mathrm{A}+\mathrm{B}\rightleftarrows\mathrm{C})$ for the equilibrium probability distribution $\mathcal{P}_e(\mathrm{A}+\mathrm{B}\rightleftarrows\mathrm{C})$ into the two parts, $S_e(\mathrm{A})$ and $S_e(\mathrm{B}(\langle\mathrm{A}\rangle)\rightleftarrows\mathrm{C})$, we have consequently

$$S(\mathrm{A}+\mathrm{B}\rightleftarrows\mathrm{C})=S(\mathrm{A})+S(\mathrm{B}(\langle\mathrm{A}\rangle)\rightleftarrows\mathrm{C}), \tag{26, A}$$

which is in a form similar to the conditional entropy in the theory of information. In writing the above equation, we have defined

$$S(\mathrm{A})=-\boldsymbol{k}\langle\ln[\mathcal{P}(\mathrm{A})/\mathcal{P}_e(\mathrm{A})]\rangle+S_e(\mathrm{A}) \tag{27}$$

and

$$\begin{aligned}&S(\mathrm{B}(\langle\mathrm{A}\rangle)\rightleftarrows\mathrm{C})\\&=-\boldsymbol{k}\langle\ln[\mathcal{P}(\mathrm{B}(\langle\mathrm{A}\rangle)\rightleftarrows\mathrm{C})/\mathcal{P}_e(\mathrm{B}(\langle\mathrm{A}\rangle)\rightleftarrows\mathrm{C})]\rangle\\&\quad+S_e(\mathrm{B}(\langle\mathrm{A}\rangle)\rightleftarrows\mathrm{C}).\end{aligned} \tag{28}$$

Proceeding in the same manner, we get also for the relation (22, B),

$$S(\mathrm{A}+\mathrm{B}\rightleftarrows\mathrm{C})=S(\mathrm{B})+S(\mathrm{A}(\langle\mathrm{B}\rangle)\rightleftarrows\mathrm{C}). \tag{26, B}$$

In order to express explicitly the stochastic entropy (26, A), we start with the evaluation of Eq. (28). Since the probability $\mathcal{P}(\mathrm{B}(\langle\mathrm{A}\rangle)\rightleftarrows\mathrm{C})$ is given by Eq. (15) and it follows that

$$\begin{aligned}&\mathcal{P}_e(\mathrm{B}(\langle\mathrm{A}\rangle)\rightleftarrows\mathrm{C})\\&=\binom{n_{\mathrm{B}}{}^{(0)}}{n_{\mathrm{C}}}(n_{\mathrm{A}}{}^{(0)}/\alpha)^{n_{\mathrm{C}}}\{(\alpha-n_{\mathrm{A}}{}^{(0)})/\alpha\}^{n^{(0)}{}_{\mathrm{B}}-n_{\mathrm{C}}},\end{aligned} \tag{29}$$

the stochastic entropy $S(\mathrm{B}(\langle\mathrm{A}\rangle)\rightleftarrows\mathrm{C})$ takes the form

$$\begin{aligned}&S(\mathrm{B}(\langle\mathrm{A}\rangle)\rightleftarrows\mathrm{C})\\&=-\boldsymbol{k}\Big\{\langle n_{\mathrm{C}}\rangle\ln\frac{n_{\mathrm{A}}{}^{(0)}(1-\exp[-\lambda(\alpha-\beta)t])}{\alpha-\beta\exp[-\lambda(\alpha-\beta)t]}\\&\quad+(n_{\mathrm{B}}{}^{(0)}-\langle n_{\mathrm{C}}\rangle)\\&\quad\times\ln\frac{\alpha-n_{\mathrm{A}}{}^{(0)}-(\beta-n_{\mathrm{A}}{}^{(0)})\exp[-\lambda(\alpha-\beta)t]}{\alpha-\beta\exp[-\lambda(\alpha-\beta)t]}\\&\quad-\langle n_{\mathrm{C}}\rangle\ln(n_{\mathrm{A}}{}^{(0)}/\alpha)-(n_{\mathrm{B}}{}^{(0)}-\langle n_{\mathrm{C}}\rangle)\\&\quad\times\ln[(\alpha-n_{\mathrm{A}}{}^{(0)})/\alpha]\Big\}+S_e(\mathrm{B}(\langle\mathrm{A}\rangle)\rightleftarrows\mathrm{C}).\end{aligned} \tag{30}$$

With the aid of the relations, $\alpha\beta=n_{\mathrm{A}}{}^{(0)}n_{\mathrm{B}}{}^{(0)}$, $\beta=\langle n_{\mathrm{C}}\rangle_{\mathrm{e}}$ and $\{\alpha+n_{\mathrm{A}}{}^{(0)}-(\beta-n_{\mathrm{A}}{}^{(0)})\exp[-\lambda(\alpha-\beta)t]\}/\{\alpha-\beta\exp[-\lambda(\alpha-\beta)t]\}=n_{\mathrm{A}}{}^{(0)}(n_{\mathrm{A}}{}^{(0)}-\langle n_{\mathrm{C}}\rangle)/\alpha\beta$, the above equation is reduced to

$$\begin{aligned}&S(\mathrm{B}(\langle\mathrm{A}\rangle)\rightleftarrows\mathrm{C})\\&=-\boldsymbol{k}\{\langle n_{\mathrm{C}}\rangle\ln(\langle n_{\mathrm{C}}\rangle/\langle n_{\mathrm{C}}\rangle_e)\\&\quad+(n_{\mathrm{B}}{}^{(0)}-\langle n_{\mathrm{C}}\rangle)\ln[(n_{\mathrm{B}}{}^{(0)}-\langle n_{\mathrm{C}}\rangle)/(n_{\mathrm{B}}{}^{(0)}-\langle n_{\mathrm{C}}\rangle_e)]\}\\&\quad+S_e(\mathrm{B}(\langle\mathrm{A}\rangle)\rightleftarrows\mathrm{C}).\end{aligned} \tag{31, A}$$

Similarly, for the modified second-order reaction (II, B), we have

$$\begin{aligned}&S(\mathrm{A}(\langle\mathrm{B}\rangle)\rightleftarrows\mathrm{C})\\&=-\boldsymbol{k}\{\langle n_{\mathrm{C}}\rangle\ln(\langle n_{\mathrm{C}}\rangle/\langle n_{\mathrm{C}}\rangle_e)\\&\quad+(n_{\mathrm{A}}{}^{(0)}-\langle n_{\mathrm{C}}\rangle)\ln[(n_{\mathrm{A}}{}^{(0)}-\langle n_{\mathrm{C}}\rangle)/(n_{\mathrm{A}}{}^{(0)}-\langle n_{\mathrm{C}}\rangle_e)]\}\\&\quad+S_e(\mathrm{A}(\langle\mathrm{B}\rangle)\rightleftarrows\mathrm{C}).\end{aligned} \tag{31, B}$$

Since Eqs. (21) and (19) correspond to the probabilities $\mathcal{P}(\mathrm{A})$ and $\mathcal{P}_e(\mathrm{A})$, respectively, we obtain from Eq. (27)

$$\begin{aligned}S(\mathrm{A})&=-\boldsymbol{k}\{\langle n_{\mathrm{A}}\rangle\ln(\langle n_{\mathrm{A}}\rangle/\langle n_{\mathrm{A}}\rangle_e)\\&\quad-(\langle n_{\mathrm{A}}\rangle-\langle n_{\mathrm{A}}\rangle_e)\}+S_e(\mathrm{A}).\end{aligned} \tag{32, A}$$

Similarly, we have for the probability $\rho(\mathrm{B})$

$$S(\mathrm{B}) = -\boldsymbol{k}\{\langle n_\mathrm{B}\rangle \ln(\langle n_\mathrm{B}\rangle/\langle n_\mathrm{B}\rangle_e) - (\langle n_\mathrm{B}\rangle - \langle n_\mathrm{B}\rangle_e)\} + S_e(\mathrm{B}). \tag{32, B}$$

In the final analysis, the substitution of Eqs. (31, A) and (32, A) into Eq. (26, A) leads to

$$\begin{aligned} S(\mathrm{A}+\mathrm{B} \rightleftarrows \mathrm{C}) &= -\boldsymbol{k}\{\langle n_\mathrm{A}\rangle \ln(\langle n_\mathrm{A}\rangle/\langle n_\mathrm{A}\rangle_e) + \langle n_\mathrm{B}\rangle \ln(\langle n_\mathrm{B}\rangle/\langle n_\mathrm{B}\rangle_e) \\ &\quad + \langle n_\mathrm{C}\rangle \ln(\langle n_\mathrm{C}\rangle/\langle n_\mathrm{C}\rangle_e) + (\langle n_\mathrm{C}\rangle - \langle n_\mathrm{C}\rangle_e)\} \\ &\quad + S_e(\mathrm{A}+\mathrm{B} \rightleftarrows \mathrm{C}), \end{aligned} \tag{33}$$

or by setting $\Delta_i S(\mathrm{A}+\mathrm{B}\rightleftarrows\mathrm{C}) = S(\mathrm{A}+\mathrm{B}\rightleftarrows\mathrm{C}) - S_e(\mathrm{A}+\mathrm{B}\rightleftarrows\mathrm{C})$,

$$\begin{aligned} \Delta_i S(\mathrm{A}+\mathrm{B} \rightleftarrows \mathrm{C}) &= -\boldsymbol{k}\{\langle n_\mathrm{A}\rangle \ln(\langle n_\mathrm{A}\rangle/\langle n_\mathrm{A}\rangle_e) + \langle n_\mathrm{B}\rangle \ln(\langle n_\mathrm{B}\rangle/\langle n_\mathrm{B}\rangle_e) \\ &\quad + \langle n_\mathrm{C}\rangle \ln(\langle n_\mathrm{C}\rangle/\langle n_\mathrm{C}\rangle_e) + (\langle n_\mathrm{C}\rangle - \langle n_\mathrm{C}\rangle_e)\}, \end{aligned} \tag{33$'$}$$

where $\langle n_\mathrm{A}\rangle = n_\mathrm{A}{}^{(0)} - \langle n_\mathrm{C}\rangle$ and $\langle n_\mathrm{B}\rangle = n_\mathrm{A}{}^{(0)} - \langle n_\mathrm{C}\rangle$ have been used. Following the same argument closely we can again find Eq. (33) from Eqs. (26, B), (31, B), and (32, B). We have therefore the symmetrization

$$\begin{aligned} S(\mathrm{A}+\mathrm{B} \rightleftarrows \mathrm{C}) &= \frac{1}{2}\{[S(\mathrm{A}) + S(\mathrm{B}(\langle\mathrm{A}\rangle) \rightleftarrows \mathrm{C})] \\ &\quad + [S(\mathrm{B}) + S(\mathrm{A}(\langle\mathrm{B}\rangle) \rightleftarrows \mathrm{C})]\} \\ &= \text{r. h. s. of Eq. (33)}. \end{aligned} \tag{34}$$

From Eq. (33), the stochastic entropy production $\sigma = \mathrm{d}S(\mathrm{A}+\mathrm{B}\rightleftarrows\mathrm{C})/\mathrm{d}t$ can be readily obtained as

$$\sigma = \boldsymbol{k}(\mathrm{d}\langle n_\mathrm{C}\rangle/\mathrm{d}t)\ln\left(\frac{\langle n_\mathrm{C}\rangle_e}{\langle n_\mathrm{A}\rangle_e\langle n_\mathrm{B}\rangle_e}\bigg/\frac{\langle n_\mathrm{C}\rangle}{\langle n_\mathrm{A}\rangle\langle n_\mathrm{B}\rangle}\right). \tag{35}$$

If it is assumed that temperature T is uniform throughout the reaction system, the chemical affinity $\boldsymbol{a}$ is expressed by

$$\begin{aligned} \boldsymbol{a} &= \boldsymbol{k}T\{\ln(\langle n_\mathrm{A}\rangle/\langle n_\mathrm{A}\rangle_e) + \ln(\langle n_\mathrm{B}\rangle/\langle n_\mathrm{B}\rangle_e) \\ &\quad - \ln(\langle n_\mathrm{C}\rangle/\langle n_\mathrm{C}\rangle_e)\} \end{aligned} \tag{36}$$

and the reaction velocity by $v = \mathrm{d}\langle n_\mathrm{C}\rangle/\mathrm{d}t$. The stochastic entropy production (35) is reduced to

$$\sigma = (\boldsymbol{a}/T)v \tag{37}$$

a form convenient for comparison with the entropy production in the usual nonequilibrium thermodynamics.[5]

It is instructive to compare the stochastic theory with the usual one. In the latter, the entropy change due to a chemical reaction $\sum_{i=1}^{r} \nu_i \mathrm{A}_i \rightleftarrows \sum_{j=1}^{p} \nu_j{}'\mathrm{A}_j{}'$ in ideal gases can be written as

$$\Delta_i S = \int_{\text{equilibrium state}}^{\text{arbitrary reaction state}} (\boldsymbol{a}/T)\mathrm{d}\xi, \tag{38}$$

where the degree of advancement ξ is defined by $-\mathrm{d}\langle n_{\mathrm{A}_i}\rangle/\nu_i = \mathrm{d}\langle n_{\mathrm{A}_j}{}'\rangle/\nu_j{}' = \mathrm{d}\xi$ and the chemical affinity $\boldsymbol{a}$ is given by

$$\begin{aligned} \boldsymbol{a} &= \sum_{i=1}^{r} \nu_i \mu_{\mathrm{A}_i} - \sum_{j=1}^{p} \nu_j{}' \mu_{\mathrm{A}_j{}'} \\ &= \boldsymbol{k}T\left\{\sum_{i=1}^{r} \nu_i \ln(\langle n_{\mathrm{A}_i}\rangle/\langle n_{\mathrm{A}_i}\rangle_e) - \sum_{j=1}^{p} \nu_{j'} \ln(\langle n_{\mathrm{A}_j{}'}\rangle/\langle n_{\mathrm{A}_j{}'}\rangle_e)\right\}. \end{aligned} \tag{39}$$

In this equation, we have used as the chemical potential of component γ,

$$\mu_\gamma = \boldsymbol{k}T\ln\langle n_\gamma\rangle + \eta_\gamma(T, V),$$

where $\langle n_\gamma\rangle$ is the mean number of molecules of reacting species γ and $\eta_\gamma(T, V)$ a function of volume V and temperature T only. After integration, we obtain

$$\begin{aligned} \Delta_i S = -\boldsymbol{k}\Big\{ &\sum_{i=1}^{r} [\langle n_{\mathrm{A}_i}\rangle \ln(\langle n_{\mathrm{A}_i}\rangle/\langle n_{\mathrm{A}_i}\rangle) - \langle n_{\mathrm{A}_i}\rangle + \langle n_{\mathrm{A}_i}\rangle_e] \\ &+ \sum_{i=1}^{p} [\langle n_{\mathrm{A}'_j}\rangle \ln(\langle n_{\mathrm{A}'_j}\rangle/\langle n_{\mathrm{A}'_j}\rangle_e) \\ &- \langle n_{\mathrm{A}'_j}\rangle + \langle n_{\mathrm{A}'_j}\rangle_e]\Big\}. \end{aligned} \tag{40}$$

In the case of reaction (I), for instance, we have Eq. (33′) by using the relation $-(\langle n_\mathrm{A}\rangle - \langle n_\mathrm{A}\rangle_e) = -(\langle n_\mathrm{B}\rangle - \langle n_\mathrm{B}\rangle_e) = \langle n_\mathrm{C}\rangle - \langle n_\mathrm{C}\rangle_e$. Reflecting upon the requirement that the mean numbers of molecules, $\langle n_{\mathrm{A}_i}\rangle$ and $\langle n_{\mathrm{A}'_j}\rangle$, have to be taken with respect to a probability distribution governing the reaction system, we may reform Eq. (40) into

$$\begin{aligned} \Delta_i S = -\boldsymbol{k}\Big\langle \ln\Big\{ &\prod_{i=1}^{r}\left(\frac{\exp(-\langle n_{\mathrm{A}_i}\rangle)\langle n_{\mathrm{A}_i}\rangle^{n_{\mathrm{A}_i}}}{n_{\mathrm{A}_i}!}\bigg/\frac{\exp(-\langle n_{\mathrm{A}_i}\rangle_e)\langle n_{\mathrm{A}_i}\rangle_e{}^{n_{\mathrm{A}_i}}}{n_{\mathrm{A}_i}!}\right) \\ &\times \prod_{j=1}^{p}\left(\frac{\exp(-\langle n_{\mathrm{A}'_j}\rangle)\langle n_{\mathrm{A}'_j}\rangle^{n_{\mathrm{A}'_j}}}{n_{\mathrm{A}'_j}!}\bigg/\frac{\exp(-\langle n_{\mathrm{A}'_j}\rangle_e)\langle n_{\mathrm{A}'_j}\rangle_e{}^{n_{\mathrm{A}'_j}}}{n_{\mathrm{A}'_j}!}\right)\Big\}\Big\rangle. \end{aligned} \tag{41}$$

Thus, it turns out that Poisson distribution holds for each reacting species and that it is maintained invariant throughout the reaction process in local equilibrium, which is also assumed in Eq. (38). If we set

$$p(n_\gamma) = \exp(-\langle n_\gamma\rangle)\langle n_\gamma\rangle^{n_\gamma}/n_\gamma! \tag{42}$$

and

$$p_e(n_\gamma) = \exp(-\langle n_\gamma\rangle_e)\langle n_\gamma\rangle_e{}^{n_\gamma}/n_\gamma! \tag{43}$$

and take the average with respect to the probability distribution $\prod_\gamma p(n_\gamma)$, we can rewrite Eq. (41) in the form

$$\begin{aligned} \Delta_i S &= -\boldsymbol{k}\sum_{\boldsymbol{n}}\prod_{\gamma} p(n_\gamma)\ln\Big(\prod_{\gamma}[p(n_\gamma)/p_e(n_\gamma)]\Big) \\ &= -\boldsymbol{k}\sum_{\gamma}\sum_{n_\gamma} p(n_\gamma)\ln[p(n_\gamma)/p_e(n_\gamma)]. \end{aligned} \tag{44}$$

If, furthermore, we set $\prod_\gamma p(n_\gamma) = P(\boldsymbol{n})$, we obtain from Eq. (44) the Gibbs entropy postulate

$$\Delta_i S = -\boldsymbol{k}\sum_{\boldsymbol{n}} P(\boldsymbol{n})\ln[P(\boldsymbol{n})/P_e(\boldsymbol{n})] \tag{45}$$

in agreement with Eq. (1). We can therefore conclude that for the entropy change due to a chemical reaction in ideal gases the thermodynamic expression (38) is equivalent to the stochastic one (1).

We can rewrite Eq. (44) corresponding to Eq. (1′) as

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[5] I. Prigogine, "Introduction to Thermodynamics of Irreversible Processes," 3rd ed., Interscience Publishers, New York (1967), p. 23.

$$S = -\boldsymbol{k} \sum_{\gamma} \sum_{n_\gamma} p(n_\gamma) \ln[p(n_\gamma)/p_e(n_\gamma)] + S_e. \tag{44'}$$

Assuming $S_e = \sum_{\gamma} S_e(\gamma)$, where $S_e(\gamma)$ denotes the entropy for the equilibrium probability distribution of reacting species γ, we obtain from Eq. (44′)

$$S = \sum_{\gamma} S(\gamma), \tag{46}$$

where

$$S(\gamma) = -\boldsymbol{k} \sum_{n_\gamma} p(n_\gamma) \ln[p(n_\gamma)/p_e(n_\gamma)] + S_e(\gamma). \tag{47}$$

This has its origin in the factorization $P(\boldsymbol{n}) = \prod_{\gamma} p(n_\gamma)$. In other words, we can say that the joint probability distribution $P(\boldsymbol{n};\, t)$ for reaction states, at all times $0 \leq t \leq \infty$, is factorized as $P(\boldsymbol{n};\, t) = \prod_{\gamma} P(n;\, t)$ in thermodynamic limit. However, so far as thermodynamic considerations are concerned, the probability distribution of reaction states can not be explicitly found through the reaction kinetics. The reason why we have presumed to use the factorization such as Eq. (22, A) or (22, B) is to formulate stochastically the nonequilibrium thermodynamics by considering at least the stochastic process of the modified reaction (II, A) or (II, B), which is of an advantage to the approximate solution of the stochastic process of reaction (I). We emphasize finally that such a theory can systematically deal with the nonequilibrium thermodynamics of chemical reaction together with its stochastic process.

The stochastic theory presented in this paper can be applied to other reactions, *e.g.*, $\mathrm{A+B \rightleftarrows C+D}$. The stochastic entropy is given by $S(\mathrm{A+B \rightleftarrows C+D}) = S(\mathrm{B}(\langle\mathrm{A}\rangle) \rightleftarrows \mathrm{C}(\langle\mathrm{D}\rangle)) + S(\mathrm{A}(\langle\mathrm{B}\rangle) \rightleftarrows \mathrm{D}(\langle\mathrm{C}\rangle))$ or $S(\mathrm{A+B \rightleftarrows C+D}) = 1/2\{[S(\mathrm{A}) + S(\mathrm{D}) + S(\mathrm{B}(\langle\mathrm{A}\rangle) \rightleftarrows \mathrm{C}(\langle\mathrm{D}\rangle))] + [S(\mathrm{B}) + S(\mathrm{C}) + S(\mathrm{A}(\langle\mathrm{B}\rangle) \rightleftarrows \mathrm{D}(\langle\mathrm{C}\rangle))]\}$. Of course, the former agrees with the latter, assuming the relation (46).