

# One Theoretical Treatment of Chemical Reaction

## Part 2 One Part of Relation to Statistical Mechanics

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### Introduction

In the Part 1 of "On Theoretical Treatment of Chemical Reaction", the application of theoretical treatment to chemical reaction in general case was published. As mentioned on the previous paper, the general material is constructed with molecule that the component is atom. The atom is constructed with various elementary particles. About the component, atom, the treatment may be reported on other paper. These objective problems are restricted with the field of molecule showing on Part 1. So, it must be mentioned that this theoretical treatment is related to statistical mechanics on the basic point. Also, the closed related point to statistical mechanics is alone described on this paper. Perhaps, it may be reported on other paper that this theoretical treatment must be related to a part of quantum mechanics on the basic point.

Statistical mechanics is necessary to analyze the mechanism of chemical reaction in company with quantum mechanics. Glasstone<sup>1)</sup> has shown the analysis of mechanism of chemical reaction using statistical mechanics reasonably. The representative excellent publication of "The Theory of Rate Processes" that was compiled creatively by him induced various important basic considerations for the chemical reaction. Especially, it contributed toward overcoming the theoretical difficulties of rate of chemical reaction. Some publications<sup>4~20)</sup> are referred to consider the concept of this theoretical treatment.

Now, some parts of the conjugated relation between statistical mechanics and chemical reaction are reported in company with quantum mechanics on this paper. At the same time, some referred basic theories and considerations consumed some space to understand these contents.

### Experimental and Results, Gedanken Experiment

Relation to statistical mechanics: The part that the theoretical treatment is related to statistical mechanics is the part of general theory developed with the method of Gibbs<sup>2)</sup> in the necessary range for understanding.

It is one object that a general mechanics presumes exactly the behavior of the system in future, when the initial state of the mechanical system is given exactly. However, it is one object that statistical mechanics presumes reasonably the behavior of the system in future, when the initial state of the mechanical system is given uncertainly.

Even if the system is a defined system that the degree of freedom is small, the method of statistical mechanics must be used in stead of general mechanics. Because the initial state of the system is given uncertainly. Moreover, the system that statistical mechanics treats predominantly is composed with a lot of chemical species. So, a general mechanics does not treat with the complex system that the degree of freedom is large. For example, it is a complex system that 11 of hydrogen gas exists at 0°C and 1 atm. Such the whole of complex system is called as an assembly that is named by Fowler<sup>3)</sup>.

Accordingly, as a statistical mechanics does not pursue

the exact change of state of the assembly in many cases, the following ensemble is considered. Namely, the ensemble has the same composition as a given real assembly. Moreover, the ensemble is an aggregation of the assembly that is distributed for the correspondence of various exact states and observations in a range. The mean change of the state of the component that composes the ensemble is investigated after the consideration. Namely, the mean property and the mean behavior of the assembly among the indicated ensemble that is distributed at the various exact states for the correspondence of the imperfect information about the initial state of the real assembly is pursued as giving the reasonable prediction against the property and the behavior of the remarked assembly. Really, according to investigate the mean property of the suitable selected representative ensemble, the regularity of the real assembly that is known empirically is possible to be interpreted sufficiently and satisfactorily. It is assumed that the mean is arithmetic mean.

Hypothesis of a priori probability: For using statistical mechanics to the assembly that the initial state is given only uncertainly, the new postulate that a general mechanics does not include has to be introduced. And, the existence of rightness of the postulate is recognized alone by the fact that the theory derived from the statistical mechanics corresponds to the experiment closely. As mentioned above, a statistical mechanics does not treat one assembly, but the aggregation of ensemble that has the same composition to the remarked assembly is considered at first. And the aggregation of ensemble that is distributed at various phases for the correspondence of the uncertain information about the state is considered in the stead of one assembly. So, the mean property of the component that is namely the representative points is investigated. For distribute the representative points to the phase that corresponds to the uncertain information of the state equally well, the assumption must be introduced as the postulate in some sort of form. For this object, the concept is assumed as follows: a priori probability that the representative points exist in the various region of the phase space is equal. Moreover, the phase space has the same dimension alone, and

corresponds to the information about the state equally well. For example, in the case of the conservative system that the having of the energy in the range between  $E$  and  $E + \delta E$  is known alone, the representative points are distributed homogeneously in the region that is corresponded to the range of the energy of the phase space, but the system is represented by microcanonical ensemble that does not be distributed in the other region. It is said that this assumption is a hypothesis of a priori probability. The deviation of one quantity from the mean value is possible to be calculated by this hypothesis. And it is known that the value is very small against the assembly. The assembly is composed with many kinds of chemical species that statistical mechanics is applied exclusively.

Distribution density: Classical statistical mechanics is set up in the only range that quantum effect is possible to be neglected. Especially, classical statistical mechanics is convenient to catch hold of a general property of statistical mechanics, and as it is simple, it is applied fairly widely at the present time. So, consider a fundamental way of thinking. Especially, the theoretical treatment of elementary reaction in the present chemical reaction theory set the base on classical statistical mechanics.

In classical mechanics, the state of the system is given by a wide sensitive position and momentum. In the case that the state of the system is decided by  $f$  pieces of momentum corresponded to  $f$  pieces of coordinate, it is said that the degree of freedom of the system is  $f$ . Now, if the state at a certain time is given, the state at a late time is decided unequivocally by knowing the property of the system and using the law of mechanics. So, it is convenient that the state of a certain system is expressed by one point of ideal Euclid-space of  $2f$  dimensions. However, if the degree of freedom of the system is  $f$ , the ideal Euclid-space has  $2f$  pieces of orthogonal axis that corresponds to each coordinate and each momentum. As the axis of the phase space, velocity  $\dot{q}_i$  does not be used, but momentum  $\dot{p}_i$  is used. Because, the quantity gives a complete satisfaction to Hamilton's equation of motion,  $\dot{q}_i = \frac{\partial H}{\partial p_i}$ ,  $\dot{p}_i = -\frac{\partial H}{\partial q_i}$ . Here,  $H$  is Hamiltonian function, and represents the total energy of the system in conservative system. It is said that the two quantities,

$q_i$  and  $p_i$ , related to this equation of motion are conjugated each other. The variable of motion that satisfies the Hamiltonian equation is called as canonical variable. And the transformation in canonical variables is called as canonical transformation. Such a space is called as phase space. The point corresponded to the state of the system is called as the representative point of the system. Also, the state of the system shown by the representative point is called as phase. The consideration that the phase space against the assembly is constructed with two kinds of space is convenient. However, the two spaces are the structural space corresponded to the one set of coordinate and the momentum space corresponded to the conjugated momentum. The phase space that is used to decide the state is given by the combination of the two kinds of space according to such a consideration. Consequently, if the phase space is used, the exact state of the one assembly at a certain time is represented as the one corresponding representative point. And the change of state of the assembly is represented as the trace that the representative point moves at that time.

The circumstances of one ensemble that is an aggregation of assembly distributed at various exact states are represented by an aggregation of such representative point. Also, it becomes that the changes of the circumstances of the ensemble are represented as the flow of the group of such a representative point.

The attentions to ensemble and phase space are mentioned to this consideration.

The first point: An assembly is constructed with many chemical species that interact each other, but an assembly that constructs an ensemble is independent each other. For example, the chemical species,  $H_2O$ , interacts each other at the state of liquid water under the condition of 1 atm and  $4^\circ C$ . But, when statistical mechanics is applied to such liquid water, its concept is considered as follows: such liquid water is constructed with ensemble of assembly that is an aggregation of such chemical species. But, each component of ensemble must be independent each other.

The second point: When an ensemble is used to statistical object, it is unnecessary to distinguish clearly between each assembly. But, the state of distribution of the representative point at various parts of the phase

space that corresponds to various exact state simply becomes alone one problem.

Consequently, if the number  $N$  of assembly that constitutes the ensemble is taken to be large enough, and if the assembly distributes continuously in phase space, the circumstances of ensemble at a certain time  $t$  are given by the density  $\rho$  that the representative point distributes in phase space. Namely,

$$\delta N = \rho (q_1, \dots, q_f, P_1, \dots, P_f, t) \delta q_1 \dots \delta q_f \delta p_1 \dots \delta p_f \quad (II-1)$$

where,  $\delta N$  is the number of component in the region of the shown differential refinement of neighborhood of the representative point  $(q_1, \dots, q_f, P_1, \dots, P_f)$ . Namely,  $\delta N$  is the number of component in the region element  $\delta q_1 \dots \delta q_f \delta P_1 \dots \delta P_f$ .

If eq. (II-1) is integrated in regard to the total phase space, the total number  $N$  of component of ensemble is given by (II-2).

$$N = \int \dots \int \rho (q, p, t) dq_1 \dots dp_f \quad (II-2)$$

The arithmetic mean value  $\bar{F} (q, p)$  of a certain mechanical quantity  $F (q, p)$  at time  $t$  is given by eq. (III-3).

$$\begin{aligned} \bar{F} (q, p) &= \frac{1}{N} \int \dots \int F (q, p) \rho (q, p, t) dq_1 \dots dp_f \\ &= \frac{\int \dots \int F (q, p) \rho (q, p, t) dq_1 \dots dp_f}{\int \dots \int \rho (q, p, t) dq_1 \dots dp_f} \quad (III-3) \end{aligned}$$

On the other hand, the density  $\rho$  does not be defined as above mentioned, but the integration in regard to the total phase space is carried on as eq. (II-4). Namely, it is often convenient that  $\rho$  is normalized in such a way. By the other expression,  $\rho = 1$  as eq. (II-4).

$$1 = \int \dots \int \rho dq_1 \dots dp_f \quad (II-4)$$

So, in such a case, eq. (II-1) and eq. (II-3) are replaced by eq. (II-5) and eq. (II-6) correspondingly.

$$\frac{\delta N}{N} = \rho \delta q_1 \dots \delta p_f \quad (II-5)$$

$$\bar{F} = \int \cdots \int F \rho dq_1 \cdots dp_f \quad (II-6)$$

Statistical equilibrium: Liouville theorem is very important to statistical mechanics in various properties related to phase space. Because, this theorem gives the time change of distribution density at the neighborhood of the given one point of phase space.

At first, when the defined region at the neighborhood of one point  $(q_1, \dots, q_f, p_1, \dots, p_f)$  of phase space is considered as follows;

$$\begin{array}{ll} q_1' < q_1 < q_1'' & p_1' < p_1 < p_1'' \\ \dots & \dots \\ q_f' < q_f < q_f'' & p_f' < p_f < p_f'' \end{array} \quad (II-7)$$

Here, symbols ' and '' mean the constant quantity. The symbolized quantity represents the constant value each one. As the difference between  $q_1''$  and  $q_1'$ ,  $q_1'' - q_1'$ , the difference between  $p_1''$  and  $p_1'$ ,  $p_1'' - p_1'$  and so on, are infinite small. And as the total number of the representative point is enough large, the number  $\delta N$  of the representative point that exists in this region element is represented according to eq. (II-1) as following;

$$\delta N = \rho (q_1'' - q_1') \cdots (q_f'' - q_f') (p_1'' - p_1') \cdots (p_f'' - p_f')$$

or as simplified form

$$\delta N = \rho \delta q_1 \cdots \delta q_f \delta p_1 \cdots \delta p_f \quad (II-8)$$

Generally, the number of representative point passed through  $2f$  pieces of surface  $q_1', \dots, q_f', p_1', \dots, p_f'$  of this region element over a certain time is different from the number of representative point passed through  $2f$  pieces of surface  $q_1'', \dots, q_f'', p_1'', \dots, p_f''$  corresponded to each surface over the same time. Therefore,  $\delta N$  changes generally with time. At first, the representative point passed through only the surface  $q_1'$  over the time  $\delta t$  exists in the range that the  $q_1$  is between  $q_1'$  and  $q_1' - \dot{q}_1 \delta t$ . Moreover, the representative point exists in the range that other  $q$  and  $p$  are defined by eq. (II-7). Consequently, the number is given by eq. (II-9) through eq. (II-8).

$$\rho \dot{q}_1 \delta t \delta q_2 \cdots \delta q_f \delta p_1 \cdots \delta p_f \quad (II-9)$$

Here,  $\rho$  and  $\dot{q}_1$  are the density at  $q_1'$  and the velocity component in  $q_1$  direction. And, as the number of representative point that passes through two surfaces of this element over the time  $\delta t$  is expressed as the term of  $\delta t^2$ . However, the representative point must pass through this component. Therefore, if  $\delta t$  is enough small, it can be neglected evidently. So, eq. (II-9) gives instantly the number of representative point that goes in and out. Namely, if  $\dot{q}_1$  is positive, the representative point is included in this element. If it is negative, its point does not be included in this element.

Likely, the number of representative point that passes through the surface  $q_1''$  over the time  $\delta t$  is expressed by eq. (II-10). However, the representative point must go in and out this element.

$$\left( \rho + \frac{\partial \rho}{\partial q_1} \delta q_1 \right) \left( \dot{q}_1 + \frac{\partial \dot{q}_1}{\partial q_1} \delta q_1 \right) \delta t \delta q_2 \cdots \delta q_f \delta p_1 \cdots \delta p_f \quad (II-10)$$

Here, if  $\dot{q}_1$  is positive, the representative point goes out the element. If it is negative, its point goes in the element. And  $\rho + \frac{\partial \rho}{\partial q_1} \delta q_1$  and  $\dot{q}_1 + \frac{\partial \dot{q}_1}{\partial q_1} \delta q_1$  are the density at  $q_1''$  and the velocity component in direction  $q_1$ . When eq. (II-9) is subtracted from eq. (II-10), the number that the representative point in the element decreases is given by the condition as follows; the representative point passes through the surfaces  $q_1'$  and  $q_1''$  over the time  $\delta t$ . Moreover, if the differential of higher order is neglected, the number is expressed as eq. (II-11).

$$\left( \rho \frac{\partial \dot{q}_1}{\partial q_1} + \dot{q}_1 \frac{\partial \rho}{\partial q_1} \right) \delta t \delta q_1 \cdots \delta p_f \quad (II-11)$$

The addition of both equations against  $f$  pieces of coordinate and  $f$  pieces of momentum gives the following equation. However the both equations are given by the same reasoning to it. The following equation points the decrease of the number of representative point in the element over the time  $\delta t$ . Namely,

$$\begin{aligned}
 -\delta N &= -\delta\rho\delta q_1\cdots\delta p_f \\
 &= \sum_{i=1}^f \left\{ \rho \left( \frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right) + \left( \frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) \right\} \delta t \delta q_1 \cdots \delta p_f
 \end{aligned}
 \tag{II-12}$$

Moreover, since canonical equation,  $\dot{q}_i = \frac{\partial H}{\partial p_i}$ ,  $\dot{p}_i = -\frac{\partial H}{\partial q_i}$  is valid,

$$\sum_{i=1}^f \left( \frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right) = 0$$

is obtained. The first term of eq. (II-12) is eliminated. Moreover, if the both sides of eq. (II-12) are divided by  $\delta t \delta q_1 \cdots \delta p_f$ ,

$$\left( \frac{\partial \rho}{\partial t} \right)_{q,p} = - \sum_{i=1}^f \left( \frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right)
 \tag{II-13}$$

is obtained.  $\left( \frac{\partial \rho}{\partial t} \right)_{q,p}$  points time differential of density  $\rho$  at the given point  $(q, p)$  of phase space.

This result means the basic importance for statistical mechanics. Often, this relation that is mentioned above is said the Liouville theorem.

Density conservation: Against the time differential  $\left( \frac{\partial \rho}{\partial t} \right)_{q,p}$  of the distribution density  $\rho$  of the representative point at one arbitrary point  $(q, p)$  of phase space, the Liouville theorem is given as eq. (II-13). Here,  $\dot{q}_i$  is the element corresponded to the degree of freedom  $i$  in the velocity that the representative point moves in the phase space,  $\dot{p}_i$  is time differential of the conjugated momentum.

The time change of  $\rho$  at the neighborhood of one moving representative point  $(q, p)$  is given by eq. (II-14), because  $\rho$  is functions of coordinate, momentum, and time.

$$\frac{d\rho}{dt} = \left( \frac{\partial \rho}{\partial t} \right)_{q,p} + \sum_{i=1}^f \left( \frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right)
 \tag{II-14}$$

Therefore, the following relation is obtained from eq. (II-13) as eq. (II-15).

$$\frac{d\rho}{dt} = 0
 \tag{II-15}$$

Namely, the density at the neighborhood of one moving

representative point does not change with time. This property of phase space is called by Gibbs as the principle of density conservation in phase.

Volume conservation: Next, consider the region element  $\delta\nu$  of phase space. If  $\delta\nu$  is enough small, the density  $\rho$  in the region can be regarded as being homogenous. Therefore, the number  $\delta N$  of the representative point in  $\delta\nu$  is given as follows,

$$\delta N = \rho \delta\nu
 \tag{II-16}$$

Now, if the boundary of this region element  $\delta\nu$  is decided usually by the same representative point, it is impossible that the representative point existed in  $\delta\nu$  disappears or appears newly. Also, if the representative point traverses the boundary, the motion can not be decided unequivocally. In other words, if the representative point traverses the boundary, it becomes that one phase does the different motion. Namely, it becomes that the two systems existed exactly at the same state do the different motion. In the field of classical mechanics, it is considered that such a phenomenon does not occur. Consequently, it is considered that such a phenomenon does not occur. Consequently, it becomes that  $\delta N$  does not change with time. Namely, from eq. (II-16),

$$\frac{d(\delta N)}{dt} = \frac{d\rho}{dt} \delta\nu + \rho \frac{d(\delta\nu)}{dt} = 0
 \tag{II-17}$$

is obtained. Therefore, from eq. (II-15)

$$\frac{d(\delta\nu)}{dt} = 0
 \tag{II-18}$$

is obtained. In consequence, the volume of the region element that the boundary is decided in such a way does not change. The concept that the same relation is set up the region of arbitrary size can be proved by the combination of such region element. This property is called by Gibbs as the principle of volume conservation in phase.

Moreover, it can be proved that the volume of region of phase space is unchangeable for the canonical transformation of coordinate. Namely, two sets of canonical variable are expressed as  $q_i, p_i$  and  $Q_i, P_i$ , the integration in regard to the same region is tried.

$$\int \cdots \int dq_1 \cdots dp_f = \int \cdots \int dQ_1 \cdots dP_f \quad (\text{II-19})$$

Therefore, without the change of size of volume, it is possible to select that  $q$  and  $p$  become coordinate and momentum of various parts of each dynamical system in general meaning. In consequence, the dimension of volume of phase space of dynamical system that the degree of freedom is  $f$  is  $(L \cdot \frac{ML}{T})^f$ . Namely, it is understood that action is raised to the  $f$ th power. These properties, eq. (II-18) and eq. (II-19), are related to quantum theory as mentioned later.

Namely, according to the uncertainty principle of Heisenberg, when the coordinate  $q_i$  and the conjugated momentum  $p_i$  are observed at the same time, the uncertainty  $\Delta$  at that time is the magnitude of action quantum  $h$  of Planck.

$$\Delta q_i \Delta p_i \sim h \quad (\text{II-20})$$

Consequently, for the dynamical system that the degree of freedom is  $f$ ,

$$\int \cdots \int dq_1 \cdots dp_f = h^f \quad (\text{II-21})$$

the region element of classical phase space that the magnitude is expressed by eq. (II-21) is regarded as the correspondence of one exact quantum state. The validity of this correspondence is recognized in various simple cases as mentioned later.

When the density  $\rho$  at the neighborhood of each point of phase space, namely the probability that exists in various parts of phase space, does not change with time, it becomes that the mean value of the property of assembly in ensemble does not change with time. The relation is understood by eq. (II-13). The assembly that is represented with such an ensemble is in statistical equilibrium. If the density  $\rho$  is constant at each point, the validity is needless to say. As can be seen from eq. (II-13), also in the case that  $\rho$  is function of constant of motion,  $\alpha$ ,

$$\left(\frac{\partial \rho}{\partial t}\right)_{q,p} = - \sum_{i=1}^f \left(\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i\right)$$

$$\begin{aligned} &= - \sum_{i=1}^f \left(\frac{\partial \rho}{\partial \alpha} \frac{\partial \alpha}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial \alpha} \frac{\partial \alpha}{\partial p_i} \frac{\partial H}{\partial q_i}\right) \\ &= 0 \end{aligned} \quad (\text{II-22})$$

The relation is expressed by eq. (II-22), so statistical equilibrium is set up.

Also, the constant of motion,  $\alpha$ , is the quantity that satisfies the following equation.

$$\begin{aligned} \frac{d\alpha}{dt} &= \sum_{i=1}^f \left(\frac{\partial \alpha}{\partial q_i} \dot{q}_i + \frac{\partial \alpha}{\partial p_i} \dot{p}_i\right) \\ &= \sum_{i=1}^f \left(\frac{\partial \alpha}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \alpha}{\partial p_i} \frac{\partial H}{\partial q_i}\right) \\ &= 0 \end{aligned} \quad (\text{II-23})$$

As the example of ensemble that represents the assembly existed at statistical equilibrium, several ensembles are shown as follows;

(1) Uniform ensemble: The representative point is distributed homogeneously in the total phase space in this ensemble. Namely,

$$\rho = \text{constant} \quad (\text{II-24})$$

(2) Microcanonical ensemble: As energy  $E$  is the constant of motion in conservative system, in this case, if  $\rho$  is the function of  $E$ , it becomes that statistical equilibrium is set up. Among such an ensemble, Boltzman used mainly microcanonical ensemble. Its ensemble is defined as follows;

$$\begin{aligned} \rho &= \text{constant} \quad (\text{in the range between } E \text{ and } E + \delta E) \\ \rho &= 0 \quad (\text{except the above described range}) \end{aligned} \quad (\text{II-25})$$

it is used to represent the assembly that energy is constant.

(3) Canonical ensemble: Another one important ensemble for conservative system is this canonical ensemble that Gibbs induced in the following expression.

$$\rho = N e^{-\frac{\varphi - E}{\theta}} \quad (\text{II-26})$$

Here,  $N$  is the total number of representative point, also

$\varphi$  and  $\theta$  are parameters that have the dimension of energy.  $\varphi$  and  $\theta$  are not independent each one.

$$N = \int \cdots \int \rho dq_1 \cdots dp_f = N \int \cdots \int e^{-\frac{\varphi - E}{\theta}} dq_1 \cdots dp_f$$

Consequently,

$$e^{-\frac{\varphi}{\theta}} = \int \cdots \int e^{-\frac{E}{\theta}} dq_1 \cdots dp_f \quad (\text{II-27})$$

Such an ensemble is suitable to represent the assembly existed at constant temperature. In consequence, if it is said that the assembly is at statistical equilibrium, in the case without notice especially, it is said that the representation ensemble is canonical generally. So, the ensemble that is objective or considerable in this case is almost this canonical ensemble.

Principle of detailed balance: Moreover, generally, it is said that statistical equilibrium can be set up by the following condition; the mean number of chemical species of assembly that shifts from one state to another state over the unit time is equal to the mean number of the same chemical species. However, the same chemical species shifts to the reverse direction. Its existence of this relation is said as the principles of detailed balance.

### Discussion and Conclusion

The duplication of contents that are mentioned in the section of Experimental and Results is cut off except the important parts from the space of this paper.

Statistical mechanics: If some specific points of general mechanics and statistical mechanics can be mentioned simply, general mechanics requires the certain initial state to predicate upon the certain future behavior and statistical mechanics does not require the certain initial state to predicate upon the certain future behavior. In consequence, statistical mechanics is useful to analyze the reaction mechanism. Then, the theoretical consideration is carried out with the statistical mechanics.

This statistical mechanics selects the assembly and the ensemble as one experimental object of Gedanken experiment.

Hypothesis of a priori probability: When the statis-

tical mechanics treats the assembly that is at the uncertain initial state, a postulate that does not be included in classical statistical mechanics must be induced as one special kind of treatment method. The special condition that microcanonical ensemble is established represents the system.

There is one case that an appearance probability of each phenomenon is defined, after an assembly is thought from the results tried many times. And, there is one case that an appearance probability of a phenomenon is decided theoretically from the condition given physically. Also, the case that there is no mechanical selectivity is thought, it is said that the induced probability in such a case is called a priori probability.

Now, the assumption is formed as follows; microscopic state that can not be identified appears in an equal probability according to the incomplete information of particle. When the assumption is included in the condition, "Principle of equal a priori probability" is recognized as an axiom. This point is very important in the object of statistical mechanics.

Distribution density: Classical statistical mechanics sets up at a negligible range, but in spite of this restrict, general property of statistical mechanics is possible to be caught comparatively easy. The consideration of classical statistical mechanics is basic point of theoretical treatment of elementary reaction in chemical reaction theory to understand this contents easy. The concept formation of consideration is trying comprehensively. And, classical mechanics requires a wide-sensitive position and momentum to the condition of state of system with degree of freedom. Adding time factor, Euclid-space is considered as a system of phase space. Phase space of assembly is constructed with structural space and momentum space. Therefore, state of assembly at a certain time is replaced by representative point, and state change of assembly is replaced by trace of moving point. So, the ensemble that is aggregation of assembly is replaced by an aggregation of representative point. Then, state change of ensemble is replaced by flow of representative point groups.

Next, an assembly is constituted with chemical species that interacts each other, but the assembly that con-

stitues the ensemble is independent each other. And each assembly is unnecessary to classify, distribution state of representative point in phase space is necessary to study. So, density or representative point in phase space is expressed by equation. Here, to be convenient, normalization method is applied. However, in other case of biological problem, complicate living matter is impossible to be normalized. From inheritance, it is very important and interest that exact normalization is not set up in one living matter itself. There is some important difference between probability and real problem, individual. One thing is different from probability based on aggregation. So, this joint may be found at molecular level, atomic level or elementary particular level of such a very complicate matter.

The above described interpretation that helps the understand may include more and less difference from exact expression by equation. The author hopes that exact understand and expression cancel this difference mentioned above.

Statistical equilibrium: Liouville theorem is useful to express the time differential of distribution density of representative point in one arbitrary point of phase space. Several factors, time, velocity, degree of freedom, and momentum, are taken in state change.

The conservation principles of density and volume proposed by Gibbs, and the uncertainty principle proposed by Heisenberg are considered as one solution method of the relation between statistical mechanics and quantum theory. So, density of representative point, probability in phase space, and change or unchange per time are considered to study the property of assembly in ensemble. Consequently, statistical equilibrium is defined and is possible to be expressed by equation. Moreover, when an ensemble represents one assembly existed at statistical equilibrium, the following defined ensembles are deduced. (1) uniform ensemble, (2) microcanonical ensemble, and (3) canonical ensemble.

In general case of these reports, the condition that the representation ensemble is canonical is meaning in the condition of the assembly existed at statistical equilibrium except a special decided noticed condition. Statistical equilibrium is also meaning in equal mean

number that chemical species of an assembly shifts forward and backward directions over unit time.

#### Reference

- 1) S. Glasstone, K. J. Laidler, H. Eyring; *The Theory of Rate Processes*, McGRAW-HILL, 1941
- 2) J. W. Gibbs; *Elementary Principles in Statistical Mechanics*, Yale Univ. Press., 1902
- 3) R. H. Fowler; *Statistical Mechanics*, Ed. 2, Cambridge, 1936
- 4) L. Pauling, E. B. Wilson; *Introduction to Quantum Mechanics*, McGRAW-HILL, 1935
- 5) R. C. Tolman; *The Principles of Statistical Mechanics*, Oxford Univ. Press., 1938
- 6) J. E. Mayer; *Statistical Mechanics*: John Wiley & Sons, 1940
- 7) A. I. Khinchin; *Mathematical Foundations of Statistical Mechanics*, Dover Pub., 1949
- 8) H. Goldstein; *Classical Mechanics*, Addison-Wesley Pub., 1950
- 9) F. W. Sears; *Thermodynamics, the Kinetic Theory of Gases, and Statistical Mechanics*, Addison-Wesley Pub., 1953
- 10) L. I. Schiff; *Quantum Mechanics*, 3rd Ed. Inter. Stu. Ed., 1955
- 11) P. A. M. Dirac; *The Principles of Quantum Mechanics*, 4th Ed., Oxford Clarendon Press., 1958
- 12) F. W. Sears; *Thermodynamics*, Addison-Wesley Pub., 1959
- 13) A. A. Frost, R. G. Pearson; *Kinetics and Mechanism*, John Wiley & Sons, 1961
- 14) E. Schrödinger; *Statistical Thermodynamics*, Cambridge Univ. Press., 1964
- 15) R. P. Feynman, A. R. Hibbs; *Quantum Mechanics and Path Integrals*, McGRAW-HILL, 1965
- 16) T. C. Bradbury; *Theoretical Mechanics*, Wiley Inter. Ed., 1968
- 17) W. Miller, H. F. Schasfer, B. J. Berne, G. A. Segal; *Modern Theoretical Chemistry*, A, B, Prentice Hall Press., 1977
- 18) D. R. Cox, P. A. W. Lewis; *The Statistical Analysis of Series of Events*, Chapman & Hall, 1978
- 19) B. H. Lavenda; *Thermodynamics of Irreversible Processes*, Macmillan Press., 1978



## One Theoretical Treatment of Chemical Reaction

20) K. Baclawski, M. D. Donsker; Mark Kac: Probability, Number Theory, and Statistical Physics, Selected Papers, MIT Press., 1979

### Summary

One part of new theoretical treatment that was related closely to statistical mechanics, quantum mechanics, and thermodynamics was published on this paper as Gedanken experiment. But, this paper is one part of series of new theoretical treatment of chemical reaction. This new consideration was induced to the combination of chemical reaction and statistical mechanics by the author as a new reasonable try.

On this paper, the relation between chemical reaction and statistical mechanics is mainly treated except the rested part related to this relation according to paper

space. Especially, the fundamental theories and concepts that are based on the field of statistical mechanics are described as a new Gedanken experiment. So, new conceptions were induced to the relation mentioned above by the author with the developments of various equations.

Therefore, the concepts were applied to the following objective problems; (1) One relation to statistical mechanics in general case, (2) Hypothesis of a priori probability, (3) Distribution density, (4) Statistical equilibrium, (5) Density conservation, (6) Volume conservation, (7) Ensemble – Uniform ensemble, Micro-canonical ensemble, Canonical ensemble, (8) Principle of detailed balance.

One rested part about the relation to statistical mechanics and other objective problems may be published on the next paper as Part 3.

### 化学反応の理論的取扱

#### 第2報 統計力学との関係

堀 津 圭 佑

統計力学、量子力学、熱力学と関係深い新理論的取扱の一部を思考実験として報告した。この報告は化学反応の新理論的取扱の一部である。この新考察は化学反応と統計力学との組合せにつき、合理的試みとして導かれた。『化学反応と統計力学との関係について紙面の都合上残された部分以外を主に取扱った。特に新思考実験として統計力学の分野に基づいた基礎的理論と概念を記した。新概念作用は種々の方程式の展開と共に前述の關係に導かれた。その概念は次の目的問題に応用された。(1)統計力学一般との關係、(2)先驗的確率の仮説、(3)分布密度、(4)統計的平衡、(5)密度保存、(6)容積保存、(7)集合一均一集合、微細正準集合、(8)詳細な釣合いの原理。』

統計力学と他の目的問題との關係に関する残された部分は次報の第3報に報告する。