

One Theoretical Treatment of Chemical Reaction

Part 5 Relation to Quantum Statistical Mechanics and Thermodynamics

Keisuke HORITSU

(Received September 29, 1984)

Introduction

The correlation between the quantity $H^{(1)}$ introduced by statistical mechanics and other quantities related to it against any quantity in thermodynamics is tried to consider at first.

The approximate and probable behavior of the assembly that is composed with a number of chemical species becomes one problem. Then, also the problem is treated naturally with the method of statistical mechanics in general case. The conditions are assumed as follows; the macro assembly is canonical ensemble and the assembly exists at thermodynamical equilibrium.

The probability against taking the Eigenvalue of energy of the assembly in the ensemble is discussed with the external parameter and the internal parameter. The quantity H in the canonical ensemble is affected by the distribution coefficient and the both parameters in the range of slight change. This discussion is performed on the way how the quantity H in the canonical ensemble changes. While the assembly is kept existing at thermodynamical equilibrium, the entropy change is considered with regard to the external parameter and the internal parameter in the case that it is made to change slightly.

In correspondence of the quantity of thermodynamics to the quantity of statistical mechanics, the relation in the both quantities can be researched.

Next, the classical approximation of Zustandsumme is considered. The number of the state must be known for calculating the Zustandsumme. In the phase space of the assembly that the degree of

freedom is decided, the regional element of a certain magnitude corresponds to one of quantum state. So, a certain region corresponds to a certain number of quantum state. The Zustandsumme is expressed in those relations.

Now, the Zustandsumme of one particle in a rectangular parallelepiped is considered. The energy of system is expressed by mass and momentum in x , y , and z directions. So, the Zustandsumme is expressed in relation to the quantum state. On the other hand, if there is no degeneracy by spin, the Zustandsumme is obtained in relation to the number of the characteristic state after the Eigenvalue of the particle is decided.

Here, the two methods of calculation are applied to obtain the Zustandsumme. Those results calculated with such different two kinds of method are equal to each one. Namely, the conclusion that the procedure of calculation is appropriate according to general consideration is possible to be recognized.

Also, the sum of Zustandsumme that is independent mechanically is expressed by the product of two parts of Zustandsumme.

And, the relation between the Zustandsumme of the macro assembly and the probability of existence at the state is discussed. And it is studied that the free energy is related to the Zustandsumme like the conjugate mean force against the Zustandsumme. The temperature change of Zustandsumme is given by the statistical mean value of energy.

One application of Zustandsumme is considered to develop this theoretical treatment.

Definition of functions; the function that is given as ratio of Zustandsumme is defined in the four types, P^δ , Q^δ_σ , $\Theta_\sigma(\delta)$, and $\Theta_\sigma(o)$ respectively.

Expansion of definition; these above described functions give a coefficient of increment of Zustandsumme by various procedures respectively. On this fundamental consideration, the four functions are expressed as one formula. Namely, $\log \lambda = \Delta \log ZC$. Then, the increment of the first order is defined at the first step. And the increment of the second order is defined at the next step. So, similarly, the increments of tertiary and more over order are possible to be defined.

Approximation; the fundamental state is decided by the appropriate procedure. The direct interaction in molecule does not affect and the increment of secondary and more over order are neglected against the increment of first order. When one procedure or another one does not decide the fundamental state, the increment that is over secondary is neglected. According to such as assumption, these following

relations are obtained. i) $\rho^{\delta_1 + \delta_2} = \rho^{\delta_1} \rho^{\delta_2}$ and $\rho^{\delta} = \frac{g}{\prod (\rho^{\delta g})^{v_g}}$. Similarly, ii) $\Theta_{\sigma(\delta)} = \frac{ZC_{\sigma(\delta)}}{ZC_0}$. Moreover,

$\Delta P_{\lambda j} \log ZC$ is expressed to power series of $\Delta \lambda P_j$ and if the term that is over secondary is neglected, iii)

$$(\Delta \lambda \log ZC)_{P+\Sigma} \frac{\partial \log ZC}{\partial P_j} \Delta \lambda P_j.$$

The correlation, $q_{\sigma}^{\delta} = \frac{\Theta_{\sigma(\delta)}}{\Theta_{\sigma(0)}} \cdot \rho^{\delta}$, of four functions, ρ^{δ} , q_{σ}^{δ} , $\Theta_{\sigma(\delta)}$, and $\Theta_{\sigma(0)}$ are obtained from the above described relation. Moreover, the following relation, $\rho^{\delta} = \frac{\Theta_{\sigma(0)} q_{\sigma}^{\delta} / |\sigma|}{\Theta_{\sigma(\delta)} / |\sigma|}$ is obtained. Here, δ is composed with only one molecule, $|\sigma|$ is volume of vacant space σ . And the other following relations are obtained respectively as follows; $N^{\delta} = \lim_{|\sigma| \rightarrow 0} \frac{\Theta_{\sigma(\delta)}}{|\sigma|}$. Here, N^{δ} is concentration of δ at astrigent point. Here, Q^{δ} is extremal value of $q_{\sigma}^{\delta} / |\sigma|$. So, the relation, $\rho^{\delta} = \frac{Q^{\delta}}{N^{\delta}}$ is obtained.

The related and refered publications¹⁻²⁶⁾ are very useful for analysis of chemical reaction to develop this new theoretical treatment.

Experimental and Results, Gedanken Experiment

Statistical mechanics and thermodynamics: in this section, at the first step, try to consider the following problem; the quantity H introduced by statistical mechanics and some other quantities related to it are corresponding to any quantity in thermodynamics or not.

The object that becomes the problem in thermodynamics is the approximate and probable behavior of the macro assembly composed with a number of chemical species as its subject described by Gibbs.¹⁾ Therefore, it is natural that the method of statistical mechanics may be possible to treat with this problem.

Now, if the macro assembly is represented with canonical ensemble, it may be assumed that the assembly exists enough at thermodynamical equilibrium. This subject is natural from the point that the canonical ensemble represents the following equilibrium system as the previous description.²⁶⁾ The equilibrium system satisfies the condition that \bar{E} is constant.

In canonical ensemble, the probability P_k that the assembly selected at random from the ensemble shows the Eigenvalue E_k of the energy of k th is given by the following equation, eq. (V - 3), from the following two equations,²⁶⁾ eq. (V - 1), and eq. (V - 2):

$$\rho_{k,l} = e^{\frac{\varphi - E_k}{\theta}} \delta_{k,l} \quad \text{therefore,} \tag{V - 1}$$

$$\rho_{k,k} = e^{-\frac{E_k}{\theta}} \tag{V - 2}$$

$$\rho_{k,k} = P_k = e^{-\frac{E_k}{\theta}} = \frac{e^{-\frac{E_k}{\theta}}}{\sum_k e^{-\frac{E_k}{\theta}}} \tag{V - 3}$$

Here, the Eigenvalue E_k of the energy is decided with several independent parameters. Also, the two kinds of classification are considered in parameter as this general fundamental consideration, die These und die Antithese,

at the first step. Like the volume occupied by the assembly, also like the electrostatic field or magnetic field that the whole assembly is existed, such subjects that macro determination is possible to perform directly are called as external parameter. Against these parameters, such a subject that macro determination is impossible to perform directly like the following description is called as internal parameter.

While the assembly is always kept existing at the statistical equilibrium, and when the distribution coefficient φ , θ , and internal and external parameters, $\alpha_1, \dots, \alpha_a, \dots$, are changed slightly, consider whether the quantity H of the canonical ensemble is subject to any change by means of the slight change.

In this case, these relations are expressed by the following equation, eq. (V - 4):

$$H = \sum_k P_k \log P_k = \sum_k e^{-\frac{\varphi - E_k}{\theta}} \frac{\varphi - E_k}{\theta} = \frac{\varphi - \bar{E}}{\theta} \quad (\text{V - 4})$$

Therefore, the relation shown in the following equation, eq. (V - 5), is obtained.

$$\delta H = \frac{\delta \varphi}{\theta} - \frac{\delta \bar{E}}{\theta} - \frac{\varphi - \bar{E}}{\theta^2} \delta \theta \quad (\text{V - 5})$$

On the other hand, as the following equation, eq. (V - 6), is valid, the following relation shown in the following equation, eq. (V - 7), is valid.

$$\sum_k P_k = \sum_k e^{-\frac{\varphi - E_k}{\theta}} = 1 \quad (\text{V - 6})$$

$$\sum_k \left\{ e^{-\frac{\varphi - E_k}{\theta}} \left(\frac{\delta \varphi}{\theta} - \frac{1}{\theta} \sum_a \frac{\partial E_k}{\partial \alpha_a} \delta \alpha_a - \frac{\varphi - E_k}{\theta^2} \delta \theta \right) \right\} = 0 \quad (\text{V - 7})$$

Namely, this relation is shown as the following equation, eq. (V - 8):

$$\frac{\delta \varphi}{\theta} + \frac{1}{\theta} \sum_a \bar{\Pi} \alpha_a \delta \alpha_a - \frac{\varphi - \bar{E}}{\theta^2} \delta \theta = 0 \quad (\text{V - 8})$$

Here, the relation shown in the following equation, eq. (V - 9), is obtained.

$$\bar{\Pi} \alpha_a = \sum_k e^{-\frac{\varphi - E_k}{\theta}} \left(-\frac{\partial E_k}{\partial \alpha_a} \right) - \frac{\sum_k e^{-\frac{E_k}{\theta}} \left(-\frac{\partial E_k}{\partial \alpha_a} \right)}{\sum_k e^{-\frac{E_k}{\theta}}} \quad (\text{V - 9})$$

The partial differential coefficient $-\frac{\partial E_k}{\partial \alpha_a}$ corresponds to the force of doing for increasing Eigenvalue E_k of energy of the k th in the assembly with parameter α_a . However, in this case, there is a condition that the assembly is not shifted to other characteristic state. $\bar{\Pi} \alpha_a$ is statistical mean of parameter α_a . From the equations, eq. (V - 5) and eq. (V - 8), the following equation, eq. (V - 10), is obtained.

$$-\delta H = \frac{\delta \bar{E}}{\theta} + \frac{1}{\theta} \sum_a \bar{\Pi} \alpha_a \delta \alpha_a \quad (\text{V - 10})$$

Whereas, the quantity corresponding to the irreversibility of natural phenomenon in thermodynamics is entropy S . And when the assembly is changed slightly at the same time that the assembly is kept existense at thermodynamical equilibrium, the following equation, eq. (V - 11), is obtained.

$$\delta S = \frac{\delta U}{T} - \frac{1}{T} \sum_a \Pi \alpha_a \delta \alpha_a \quad (\text{V - 11})$$

Here, U is internal energy, T is thermodynamic temperature, and $\Pi \alpha_a$ is the conjugate force to external parameter α_a . Generally, in thermodynamics the subjects that give rise to discussion are volume and pressure. The pressure is the conjugate force of it. Consequently, in the equation of statistical mechanics, eq. (V - 10), if the following case is considered, these two equations, eq. (V - 10) and eq. (V - 11), become the corresponding form. The following case includes the two conditions. Namely, the internal parameter is not changed, but the external parameter only is changed.

As the quantity of thermodynamics can correspond to the quantity of statistical mechanics according to eq. (V - 12), if the relation between the quantity S that represents the irreversibility and H is assumed as the following equation, eq. (V - 13), the theoretical treat-

ment that the relation between T and θ is induced as the following equation, eq. (V - 14), is more reasonable.

$$U = E, \quad \Pi \alpha_a = \bar{\Pi} \alpha_a, \quad \alpha_a = \alpha_a \quad (V - 12)$$

$$S = -kH \quad (V - 13)$$

$$T = \frac{\theta}{k} \quad (V - 14)$$

Here, the proportional constant k is called as Boltzman's constant.

It is known as follows; it is equal to the quantity that gas constant R is divided by Avogadro's number N_A .

If the free energy F of Helmholtz is represented by the quantity of statistical mechanics according to the above described formula, the relation is shown as the following equation, eq. (V - 15):

$$F = U - TS = \bar{E} + \theta H \quad (V - 15)$$

If eq. (V - 4) is substituted to eq. (V - 15), the relation shown as the following equation, eq. (V - 16), is obtained.

$$F = \varphi \quad (V - 16)$$

And from eq. (V - 2), the following relation is obtained as shown in the following equation, eq. (V - 17):

$$F = \varphi = -\theta \log \sum_k e^{-\frac{E_k}{\theta}} = -kT \log \sum_k e^{-\frac{E_k}{kT}} \quad (V - 17)$$

Zustandsumme, Partition function: one classical approximation about Zustandsumme is considered at the first step. At first, the number of the state must be known to calculate the Zustandsumme.

Like the fundamental partial consideration was described ready on the section of statistical equilibrium²⁵⁾ and Liouville theorem, in the phase space of the assembly C that the degree of freedom is f , the regional element corresponds to one quantum state. But there is one limitation that the magnitude of the regional element is h^f . Consequently, if the exchange γ of the equivalent atom and the equivalent atomic group in the assembly is not determined independently, the region $\Delta q_1, \dots, \Delta q_f, \Delta p_1, \dots, \Delta p_f$ corresponds to

$\frac{\Delta q_1, \dots, \Delta q_f, \Delta p_1, \dots, \Delta p_f}{\gamma h^f}$ pieces of the quantum state.

Therefore, Zustandsumme ZC is given as the following equation, eq. (V - 18):

$$ZC = \frac{\int \dots \int e^{-\frac{E}{kT}} dq_1, \dots, dq_f dp_1, \dots, dp_f}{\gamma h^f} \quad (V - 18)$$

Here, the integration is carried out in regard to the total phase space that is suited to the objective condition.

Consider the Zustandsumme of one piece of molecule that is not affected by the external force in the rectangular parallelepiped. But the length of each side of the rectangular parallelepiped is $a, b,$ and c respectively. At first, the energy E of this system is given by the following equation, eq. (V - 19):

$$E = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2) \quad (V - 19)$$

Here, $p_x, p_y,$ and p_z are the momenta of the direction $x, y,$ and z respectively. In this case, as r is equal to 1, $r = 1,$ and f is equal to 3, $f = 3,$ the Zustandsumme is expressed by the following equation, eq. (V - 21), according to eq. (V - 19) and the following equation, eq. (V - 20):

$$\int_{-\infty}^{+\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}} \quad (V - 20)$$

$$ZC = \frac{\int_0^a \int_0^b \int_0^c \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{-\frac{(p_x^2 + p_y^2 + p_z^2)}{2mkT}} dx dy dz dp_x dp_y dp_z}{h^3}$$

$$\begin{aligned} &= \frac{a b c}{h^3} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{-\frac{(p_x^2 + p_y^2 + p_z^2)}{2mkT}} dp_x dp_y dp_z \\ &= \frac{v}{h^3} (2\pi mkT)^{\frac{3}{2}} \end{aligned} \quad (V - 21)$$

On the other hand, the Eigenvalue En_1, n_2, n_3 ⁷⁾ of energy of the particle is expressed by the following equation, eq. (V - 23), according to the following equation, eq. (V - 22).

$$E = \frac{h^2}{8m} \left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2} \right) \quad (V - 22)$$

$$En_1, n_2, n_3 = \frac{h^2}{m} \left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2} \right) \quad (V - 23)$$

Then, if E is large enough and if there is no degeneracy affected by spin, the number of the characteristic state existing between the range E and the range $E + dE$ is expressed by the following relation, (V - 24):

$$\frac{4\pi v}{h^3} m \sqrt{2mE} dE \quad (V - 24)$$

Therefore, the Zustandsumme is expressed by the following equation, eq. (V - 26) according to the following equation, eq. (V - 25):

$$\int_0^\infty \sqrt{x} e^{-ax} dx = \frac{1}{2} \sqrt{\frac{\pi}{a^2}} \quad (V - 25)$$

$$Z_C = \int_0^\infty \frac{4\pi v}{h^3} m \sqrt{2mE} e^{-\frac{E}{kT}} dE = \frac{v}{h^3} (2\pi mkT)^{\frac{3}{2}} \quad (V - 26)$$

Namely, in this case, the two Zustandsumme that are calculated by the two methods lead an equal result. Then, the appropriateness of eq. (V - 18) can be recognized.

Moreover, the Zustandsumme $Z(A + B)$ of $A + B$ that is composed with the independent assembly A and B is expressed by the following, eq. (V - 27). But the assembly A is independent of the assembly B dynamicaly.

$$\begin{aligned} Z(A+B) &= \sum_k e^{-\frac{E_k}{kT}} = \sum_{l,m} e^{-\frac{E_{Al} + E_{Bm}}{kT}} \\ &= \sum_l e^{-\frac{E_{Al}}{kT}} \sum_m e^{-\frac{E_{Bm}}{kT}} = Z_A \cdot Z_B \quad (V - 27) \end{aligned}$$

Namely, the $Z(A+B)$ is given as the product of two parts of Zustandsumme. Here, E_k , E_{Al} , or E_{Bm} is the Eigen-

value of energy of the assembly $A + B$, A , or B respectively.

In regard to rate of elementary reaction²³⁾, the chance that the representative point passes through the critical surface s is given by the N_s'/N_s . Now, the number A and the number B are defined respectively as follows: the number A is the number of the representative point that completes the elementary reaction. The number B is the number of the representative point that passes through the surface s from the side of initial region. Consequently, if the ratio of the number A to the number B is expressed with κ , the chance of the elementary reaction, N_1'/N_1 , is given by the following equation eq. (V - 28):

$$\frac{N_1'}{N_1} = \kappa \frac{N_s'}{N_s} = \kappa kT \frac{\int_s e^{-\frac{E^*}{kT}} dq_2 \dots dq_f dp_2 \dots dp_f}{\int_I e^{-\frac{E}{kT}} dq_1 \dots dq_f dp_1 \dots dp_f} \quad (V - 28)$$

Then, eq. (V - 28) is also expressed by the usage of the Zustandsumme of the assembly $C_0^{\delta^*}$ and the assembly $C_0^{\delta I}$. However, it is the assembly $C_0^{\delta^*}$ that the critical complex δ^* is added to the macro assembly C_0 composed with a constant chemical composition. And it is the assembly $C_0^{\delta I}$ that the initial complex δI is added to the macro assembly C_0 . The critical complex is one reacting complex that is confined to the surface s . And it is regarded that the chemical composition of C_0^{δ} is the same as that of C_0 essentially. These Zustandsumme of these assemblies are expressed by the following equations, eq. (V - 29) and eq. (V - 30), respectively according to eq. (V - 18):

$$ZC_0^{\delta^*} = \frac{\int_s e^{-\frac{E^*}{kT}} dq_2 \dots dq_f dp_2 \dots dp_f}{\gamma h^{f-1}} \quad (V - 29)$$

and

$$ZC_0^{\delta I} = \frac{\int_I e^{-\frac{E}{kT}} dq_1 \dots dq_f dp_1 \dots dp_f}{\gamma h^f} \quad (V - 30)$$

Therefore, the following relation expressed by the following equation, eq. (V - 31), is led as the result:

$$\frac{N_1'}{N_1} = \kappa \frac{kT}{h} \frac{\gamma^*}{\gamma} \frac{ZC^{\delta^*}}{ZC^{\delta_I}} \quad (\text{V} - 31)$$

However, γ^* is the number of exchange of the equivalent atom and the equivalent atomic group, in the internal part of the reacting complex and the internal part of the residual part of the assembly. But the reacting complex is confined to the surface s . And γ is the similar number with regard to the whole assembly in the case that the reacting complex exists in the initial region.

As it is assumed that the individual elementary reaction occurs independently, if the chance of the individual element reaction that is given by eq. (V - 31) is added to all possible combinations of the elementary reaction, the rate of elementary reaction of the kind in the assembly can be obtained. However, in one kind of elementary reaction, the number of all possible combinations of reacting complex is the number γ' of exchange of the equivalent atom and the equivalent atomic group between the reacting complex and the residual part of the assembly.

In consequence, the rate \vec{v} of forward direction is given by the following equation, eq. (V - 32):

$$\vec{v} = \gamma' \frac{N_1'}{N_1} = \kappa \frac{kT}{h} \frac{\gamma' \gamma^*}{\gamma} \frac{ZC_0^{\delta^*}}{ZC_a^{\delta_I}} \quad (\text{V} - 32)$$

However, as it is apparent that $\gamma' \gamma^*$ is equal to γ , $\gamma' \gamma^* = \gamma$, from the definition, the following relation is obtained as shown in the following equation, eq. (V - 33):

$$\vec{v} = \kappa \frac{kT}{h} \frac{ZC_0^{\delta^*}}{ZC_0^{\delta_I}} \quad (\text{V} - 33)$$

According to the entire similar reasoning, the rate \overleftarrow{v} of the backward direction is given by the following equation, eq. (V - 34):

$$\overleftarrow{v} = \kappa \frac{kT}{h} \frac{ZC_0^{\delta^*}}{ZC_0^{\delta_F}} \quad (\text{V} - 34)$$

Here, $ZC_0^{\delta_F}$ is the Zustandsumme that is obtained with the addition of the final complex δ_F to the assembly C_0 of constant chemical composition.

Moreover, the transmission coefficient κ in the forward and backward reactions is equal with each one. Because, as it is assumed that the assembly exists at statistical equilibrium, the number of the representative point passed through the critical surface is equal to the number of the representative point moved from one region to other region in the forward and backward reactions respectively, according to the principle of detailed balance.

On the other hand, as the above described equations, eq. (V - 33) and eq. (V - 34), are led complete independently from the relation of the entire equilibrium between the initial complex and the critical complex, generally it can be suitable to apply to the assembly existed at thermal equilibrium. And the range that can apply is not limited in the special case. The special case is the one that the reacting complex behaves independently to the other part of the assembly mechanically.

As shown later, these equations include the equations of Eyring⁴⁾, Evans and Polanyi⁵⁾ as the special case.

Next, the consideration of Zustandsumme is tried to develop this theoretical treatment step by step.

The quantity $e^{-\frac{\varphi}{\theta}}$ shown in the above described section, namely $\sum_k e^{-\frac{E_k}{\theta}}$, is called as Zustandsumme.

And $e^{-\frac{E_k}{\theta}}$ is called as Boltzmann's factor. Then, this summation is calculated for all characteristic state k of energy that the assembly is possible to exist. If the Zustandsumme of the macro assembly C is represented with ZC , the probability P_k that the assembly exists at the state k is possible to obtain from eq. (V - 3) as the following equation, eq. (V - 35):

$$P_k = \frac{e^{-\frac{E_k}{kT}}}{ZC} \quad (\text{V} - 35)$$

Also, the free energy F is expressed as the following equation, eq. (V - 36), from eq. (V - 17):

$$F = -kT \log ZC \quad (\text{V} - 36)$$

And the conjugate mean force $\bar{\Pi}\alpha_a$ to α_a is expressed as the following equation, eq. (V - 37), from eq. (V - 9):

$$\bar{\Pi}\alpha_a = \frac{\partial \log ZC}{\partial \alpha_a} \quad (\text{V} - 37)$$

Moreover, when the external parameter is unchanged, the thermal change of ZC is given by statistical mean value \bar{E} of energy as known well enough. Namely, these relations are expressed by the following equation, eq. (V - 38):

$$kT^2 \frac{\partial \log ZC}{\partial T} = \frac{\sum_k E_k e^{-\frac{E_k}{kT}}}{\sum_k e^{-\frac{E_k}{kT}}} = \bar{E} = U \quad (\text{V} - 38)$$

The objective assembly that is treated with this theoretical treatment exists mainly at constant temperature. Such an assembly is expressed by canonical ensemble. Consequently, the various properties of such an assembly are given with as usage of these Zustandsumme. In other words, the statistical mechanical properties of the assembly that the temperature is constant can be calculated if the Zustandsumme can be known. So, using the Zustandsumme of the assembly that exists at various micro conditions, the four statistical mechanical quantities are possible to be defined. These four quantities that may be explained are related to each other. Then, according to the results that the four quantities were studied, the equilibrium and the chemical reaction are possible to be studied using the in functions.

Functions; \mathcal{P}^δ , $\mathcal{Q}_{\sigma}^\delta$, $\mathcal{H}_{\sigma(\delta)}$, and $\mathcal{H}_{\sigma(o)}$: (1) Definitions of \mathcal{P}^δ , $\mathcal{Q}_{\sigma}^\delta$, $\mathcal{H}_{\sigma(\delta)}$, and $\mathcal{H}_{\sigma(o)}$: at first, the four functions that are obtained as the ratio of Zustandsumme are defined as following; the function \mathcal{P}^δ is defined by the following equation, eq. (V - 39):

$$\mathcal{P}^\delta = \frac{ZC_o^\delta}{ZC_o} \quad (\text{V} - 39)$$

Here, ZC_o is the Zustandsumme of the assembly C_o that is not permitted by micro limitation. And ZC_o^δ is the

Zustandsumme that is obtained by addition of one piece of molecule δ or a set of molecule δ into the C_o without a change of external parameter.

Second, the function $\mathcal{Q}_{\sigma}^\delta$ is defined by the following equation, eq. (V - 40):

$$\mathcal{Q}_{\sigma}^\delta = \frac{ZC_{\sigma(\delta)}^\delta}{ZC_{\sigma(o)}} \quad (\text{V} - 40)$$

Here, $ZC_{\sigma(\delta)}^\delta$ is the Zustandsumme permitted by micro limitation that one piece of molecule δ or each one of a set of molecule δ must individually exist in one state. The one state is permitted in one fundamental state σ or a set of fundamental state σ . And $ZC_{\sigma(o)}$ is the Zustandsumme of the assembly $C_{\sigma(o)}$ permitted by micro limitation that δ does not have to exist in the fundamental state σ . Then, the fundamental state σ is similar to the quantum state against the small volume, the energy of molecule, or the momentum that decides the position of center of mass of the molecule. The small volume is the same extent as magnitude to the molecule.

The following two quantities expressed by the following equations, eq. (V - 41) and eq. (V - 42), are defined with usage of the Zustandsumme appeared in both eq. (V - 39) and eq. (V - 40):

$$\mathcal{H}_{\sigma(\delta)} = \frac{ZC_{\sigma(\delta)}^\delta}{ZC_o^\delta} \quad (\text{V} - 41)$$

$$\mathcal{H}_{\sigma(o)} = \frac{ZC_{\sigma(o)}}{ZC_o} \quad (\text{V} - 42)$$

So, the following two explanations are evident from eq. (V - 35).

- $\mathcal{H}_{\sigma(\delta)}$ is the probability that δ exists at the state σ in the assembly C^δ .
- $\mathcal{H}_{\sigma(o)}$ is the probability that δ does not exist at the state σ in the assembly C .

(2) Expansion of definition: the defined four functions give the coefficient of increment of Zustandsumme caused by individual procedure. Namely, \mathcal{P}^δ is the coefficient of increment of Zustandsumme, when the C_o^δ that the component is more δ pieces than the assembly C_o is made by addition of δ . However, the assembly C_o^δ is not permitted by micro limitation like the assem-

bly C_0 . Also, q_σ^δ is the coefficient of increment of Zustandsumme when δ is added to the vacant space σ of $C_{\sigma(o)}$ from the outside of the assembly. $\Theta_{\sigma(\delta)}$ or $\bar{\Theta}_{\sigma(o)}$ is the probability in the case that certainly respectively at the decided state σ δ exists or does not exist in the assembly C_0^δ or C_0 . However, the assembly C_0^δ or C_0 is not permitted by micro limitation. The existence or nonexistence of δ at σ is an important limitation.

If the contents are understood similarly, also the four functions, p^δ , q_σ^δ , $\Theta_{\sigma(\delta)}$, and $\bar{\Theta}_{\sigma(o)}$, which are defined as the above description can be changed as the following equations, from eq. (V - 43) to eq. (V - 46):

$$\log p^\delta = \Delta p_\delta \log ZC_0 \quad (V - 43)$$

$$\log q_\sigma^\delta = \Delta q_{\sigma(\delta)} \log ZC_{\sigma(o)} \quad (V - 44)$$

$$\log \Theta_{\sigma(\delta)} = \Delta \theta_{\sigma(\delta)} \log ZC_0^\delta \quad (V - 45)$$

$$\log \bar{\Theta}_{\sigma(o)} = \Delta \theta_{\sigma(o)} \log ZC_0 \quad (V - 46)$$

Namely, if these relations are reviewed, the following equation, eq. (V - 47), is obtained:

$$\log \lambda = \Delta_\lambda \log ZC \quad (V - 47)$$

Here, λ is p^δ , q_σ^δ , $\Theta_{\sigma(\delta)}$, or $\bar{\Theta}_{\sigma(o)}$. And $\Delta_\lambda \log ZC$ is the increment of $\log ZC$ depending upon the suitable procedure that is connected with λ . Of course, for the quantity $\Delta_\lambda \log ZC$ has the physical meaning, the procedure that is connected with λ must be accessible to the objective assembly C . For example, the assembly C_0 is not permitted by any micro limitation. Moreover, if the procedure is possible to operate like δ does not exist certainly at the state σ of this assembly C_0 , it is possible that the $\bar{\Theta}_{\sigma(o)}$ can have the physical meaning.

The increment of one property P produced by the operation of the procedure that is connected with λ is expressed with $\Delta_\lambda P$. Also, without such above described imaginary procedure λ , the increment of $\log ZC$ produced by increasing of the quantity $\Delta_\lambda P$ against only P is expressed with $\Delta p_\lambda \log ZC$.

The two kinds of increment Δ defined here is the primary increment. As the two arbitrary quantities of these quantities Δ are expressed with Δ_1 and Δ_2 respectively, the secondary increments are defined as the fol-

lowing equations, eq. (V - 48) and eq. (V - 49), respectively:

$$\Delta_1 \Delta_2 \log ZC \equiv \Delta_1 \log ZC(\Delta_2) - \Delta_1 \log ZC \quad (V - 48)$$

and

$$\Delta_1 \Delta_2 P \equiv \Delta_1 P(\Delta_2) - \Delta_1 P \quad (V - 49)$$

Here, $C(\Delta_2)$ is the assembly that is produced with the procedure related to Δ_2 against C . And $P(\Delta_2)$ is the value obtained by the operation of procedure Δ_2 against P .

The higher order increment that is over tertiary is defined similarly.

(3) Approximation to definition: the objective two procedures are similar to $\Delta_1 \equiv \Delta \theta_1 \sigma_1(\delta)$ and $\Delta_2 \equiv \Delta \theta_2 \sigma_2(\delta)$. And the fundamental states, σ_1 and σ_2 , are decided by these procedures. Also, the increment that is over secondary is assumed to be neglected against the primary increment in another case, except the case that the intermolecular direct interaction existing in each one becomes objective. When this consideration is developed, one thermodynamical result obtained from this proposal can be expressed by the following equation, eq. (V - 50):

$$\mu^\delta = \sum_g \nu_g \mu_g^\delta \quad (V - 50)$$

Here, μ^δ is chemical potential, ν expresses a number of piece. δ is composed with $\delta_1, \dots, \delta_g, \dots$ kinds and $\nu_1, \dots, \nu_g, \dots$ pieces of molecule respectively. This detailed relation may be published on the next publication.

Also, the one procedure or the both procedures are similar to Δp_δ . And, when the fundamental state is not decided by the procedure, of course, the increment that is over secondary is assumed to be neglected.

If such an assumption is recognized, the following relation as shown in the following equation, eq. (V - 51), is obtained:

$$(i) \Delta p_2 (\log ZC_0 + \Delta p_{\delta_1} \log ZC_0) = \Delta p_2 \log ZC_0 \quad (V - 51)$$

And, according to eq. (V - 39) and eq. (V - 43), the following relation is led as shown in the following equation, eq. (V - 52):

$$\log ZC_0 + \Delta p_{\delta_1} \log ZC_0 = \log ZC_0^{\delta_1} \quad (V - 52)$$

Consequently, the following relation as shown in the following equation, eq. (V - 53), is led:

$$\frac{ZC_0^{\delta_1 + \delta_2}}{ZC_0^{\delta_1}} = \frac{ZC_0^{\delta}}{ZC_0} \quad (V - 53)$$

The $\rho^{\delta_1 + \delta_2}$ against one set of molecule $\delta_1 + \delta_2$ is expressed as shown in the following equation, eq. (V - 54), according to eq. (V - 39):

$$\rho^{\delta_1 + \delta_2} = \frac{ZC_0^{\delta_1 + \delta_2}}{ZC_0} = \frac{ZC_0^{\delta_1 + \delta_2}}{ZC_0^{\delta_1}} \frac{ZC_0^{\delta_1}}{ZC_0} \quad (V - 54)$$

Therefore, the following relation is obtained as shown in the following equation, eq. (V - 55):

$$\rho^{\delta_1 + \delta_2} = \rho^{\delta_1} \rho^{\delta_2} \quad (V - 55)$$

When δ is composed with the molecule that are $\nu_1, \dots, \nu_g, \dots$ pieces and $\delta_1, \dots, \delta_g, \dots$ kinds respectively, namely, when the relation can be expressed as shown in the following equation, eq. (V - 56):

$$\delta = \sum_g \nu_g \delta_g \quad (V - 56)$$

The following relation as shown in the following equation, eq. (V - 57), can be proved similarly:

$$\rho^{\delta} = \prod_g (\rho^{\delta_g})^{\nu_g} \quad (V - 57)$$

(ii) Like the above described case, the following relation is obtained as shown in the following equation, eq. (V - 58):

$$\Delta_{\theta\sigma(\delta)} (\log ZC_0 + \Delta_P \delta \log ZC_0) = \Delta_{\sigma(\delta)} \log ZC_0 \quad (V - 58)$$

In consequence, according to eq. (V - 43), the following equation, eq. (V - 59), is obtained:

$$\Delta_{\theta\sigma(\delta)} \log ZC_0^{\delta} = \Delta_{\theta\sigma(\delta)} \log ZC_0 \quad (V - 59)$$

Therefore, according to eq. (V - 41) and eq. (V - 45), the following relation as shown in the following equation, eq. (V - 60), is obtained:

$$\Theta_{\sigma(\delta)} = \frac{ZC_{\sigma(\delta)}^{\delta}}{ZC_0^{\delta}} = \frac{ZC_{\sigma(\delta)}}{ZC_0} \quad (V - 60)$$

(iii) The arbitrary increment of $\log ZC$ can be expressed as shown in the following equation, eq. (V - 61):

$$\Delta \log ZC = (\Delta_{\lambda} \log ZC)_P + \sum_j \Delta_P \lambda_j \log ZC \quad (V - 61)$$

Here, $(\Delta_{\lambda} \log ZC)_P$ is the increment in the case that the whole one of the objective property P_j is not changeable. Also, if $\Delta_P \lambda_j \log ZC$ is expanded to the power series of $\Delta_{\lambda} P_j$ and if the term that is over secondary is neglected, the following relation is obtained as shown in the following equation, eq. (V - 62):

$$\Delta_P \lambda_j \log ZC = \frac{\partial \log ZC}{\partial P_j} \Delta_{\lambda} P_j \quad (V - 62)$$

Consequently, the following relation as shown in the following equation, eq. (V - 63), is obtained:

$$\Delta_{\lambda} \log ZC = (\Delta_{\lambda} \log ZC)_P + \sum_j \frac{\partial \log ZC}{\partial P_j} \Delta_{\lambda} P_j \quad (V - 63)$$

The correlation with P^{δ} , q_{σ}^{δ} , $\Theta_{\sigma(\delta)}$, and $\Theta_{\sigma(o)}$: the following relation as shown in the following equation, eq. (V - 64), is led immediately from the equations, eq. (V - 39), eq. (V - 40), eq. (V - 41), and eq. (V - 42):

$$q_{\sigma}^{\delta} = \frac{\Theta_{\sigma(\delta)}}{\Theta_{\sigma(o)}} P^{\delta} \quad (V - 64)$$

The one case is considered as follows: δ is composed with only one molecule, and σ is almost the same magnitude of vacant space against the molecule that decides the position of the center of mass of δ . In the above described case, eq. (V - 64) can be rewritten as the following equation, eq. (V - 65):

$$\rho^{\delta} = \Theta_{\sigma(o)} \frac{q_{\sigma}^{\delta} / |\sigma|}{\Theta_{\sigma(\delta)} / |\sigma|} \quad (V - 65)$$

Here, $|\sigma|$ is volume of vacant space σ . When $|\sigma|$ approaches to 0, $ZC_{\sigma(o)}$ becomes equal to ZC_0 . In consequence, $\Theta_{\sigma(o)}$ becomes 1. And, as $\Theta_{\sigma(\delta)} / |\sigma|$ is the ratio of the probability that the center of mass of the molecule δ is in the vacant space δ to the volume of the vacant space, if the concentration of δ at the astringent point is expressed by N^{δ} when $|\sigma|$ approaches to 0, the following relation as shown in the following equation, eq. (V - 66), is obtained:

$$|N^\delta = \lim_{|\sigma| \rightarrow 0} \frac{\Theta(\sigma(\delta))}{|\sigma|} \quad (V - 66)$$

So that, as it is defined that $|P^\delta$ is independent on the volume $|\sigma|$ of the vacant space, when $|\sigma|$ approaches to 0, $q_\sigma^\delta/|\sigma|$ approaches to one constant value with $\Theta(\sigma(\delta))/|\sigma|$. If the extremal value of $q_\sigma^\delta/|\sigma|$ is expressed by Q^δ as shown in the following equation, eq. (V - 67), the following relation as shown in the following equation, eq. (V - 68), is obtained from eq. (V - 65):

$$Q^\delta = \lim_{|\sigma| \rightarrow 0} \frac{q_\sigma^\delta}{|\sigma|} \quad (V - 67)$$

$$|P^\delta = \frac{Q^\delta}{|N^\delta|} \quad (V - 68)$$

Discussion and Conclusion

New theoretical treatment is tried to apply to statistical mechanics and thermodynamics.

Statistical mechanics and thermodynamics: one quantity H is considered to be introduced from statistical mechanics. Also, the other several quantities related to this quantity are considered on the base of statistical mechanical consideration. Then, consider whether any quantity in thermodynamics corresponds to the above described quantities or not. The object of this consideration plays an important role in researching the relation between statistical mechanics and thermodynamics.

Then, as Gibbs reported previously, the subject that comes into question in thermodynamics is the approximate and probable behavior of the macro assembly. However, one condition is set to develop this theoretical treatment to general case. Namely, the macro assembly is composed with a number of chemical species. In consequence, it is considered easy that such a problem may be possible to be treated by the method of statistical mechanics. Now, if the macro assembly is represented by canonical ensemble, the following condition that the assembly exists well at thermodynamical equilibrium may be assumed. As the previous description showed

the relation to quantum statistical mechanics, canonical ensemble represents the equilibrium system that \bar{E} is constant. Then, from the consideration about the canonical ensemble, the condition of existence of the assembly may be possible to be led easily and naturally as one theoretical treatment. In such a canonical en-

semble, density matrix $\rho_{k,l}$ is equal to $e^{-\frac{\varphi - E_k}{\theta}} \delta_{k,l}$.

So, $\rho_{k,k}$ is equal to $e^{-\frac{\varphi - E_k}{\theta}}$. Here, the diagonal ele-

ment $\rho_{k,k}$ of the matrix $\rho_{k,l}$ is the probability that the one assembly selected at random from the ensemble exists at state k . In consequence, in regard to the quantity $\rho_{k,k}$ against the ensemble the following relation, $\sum_k \rho_{k,k} = \sum_k \bar{W}_k = \sum_k a_k^* a_k = 1$ is valid. There-

fore, $\sum_k \rho_{k,k} = \sum_k e^{-\frac{\varphi - E_k}{\theta}} = 1$ is set up. So that, the

relation of the parameter of distribution φ and θ is expressed by the following relation, $e^{-\frac{\varphi}{\theta}} = \sum_k e^{-\frac{E_k}{\theta}}$

According to this process of development, when the assembly is selected at random from the ensemble, the probability that the assembly shows the Eigenvalue E_k of energy of k th is expressed by eq. (V - 3). E_k is decided by several independent parameters. Generally, the two kinds of parameter are decided according to a large classification.

And, consider whether any change in the quantity H of canonical ensemble produced by the slight change of distribution coefficient, external parameter, and internal parameter or not. The quantity H is related to distribution coefficient and statistical mean value of energy of representative ensemble. And the coarse-grained density P_k is arithmetic mean value of the probability that the assembly in the ensemble exists at one of the contiguous g pieces, and is equal to 1.

According to the above described process in Experimental and Results, $-\delta H = \frac{\delta \bar{E}}{\theta} + \frac{1}{\theta} \sum_a \bar{\Pi} \alpha_a \delta \alpha_a$ is

derived. Here, $\bar{\Pi}\alpha_a$ is statistical mean of this force that the partial differential coefficient makes Eigenvalue of the assembly increase with parameter, and is the force of conjugate mean of parameter α_a .

Next, in themodynamics, the irreversibility of natural phenomena can correspond to entropy S when the assembly is changed slightly keeping the assembly existing at thermodynamical equilibrium, the following relation,

$$\delta S = \frac{\delta U}{T} - \frac{1}{T} \sum_a \Pi \alpha_a \delta \alpha_a \text{ is obtained. Here, } U,$$

T , and $\Pi\alpha_a$ are internal energy, thermodynamic temperature, and the conjugate force of external parameter α_a . Then, the quantities in equation derived from statistical mechanics can correspond to the quantities in equation derived from thermodynamics. $S = -kH$ and

$T = \frac{\theta}{k}$ are derived reasonably. Here, k is proportional

constant that gas constant is divided by Avogadro's number. Then, free energy of Helmholtz F is expressed by the quantity in statistical mechanics. At last, the

relation, $F = -kT \log \sum_k e^{-\frac{E_k}{kT}}$ is obtained. Namely, the relevancy between statistical mechanics and thermodynamics is possible to be derived, though the range is limited. The connection between them is succeeded by this method.

Zustandsumme: try to consider the classical approximation of the Zustandsumme at the first step, because, this basic understanding of the physical meaning of Zustandsumme affects to make this theoretical treatment develop. Then, as the previous description about statistical equilibrium, when the property of the assembly comes into question at least, the degree of freedom of the assembly must be considered at first. And, the phase space of the assembly is considered. Moreover, one regional element corresponds to the one quantum state. So, if the following conditions, "a) the degree of freedom of the assembly C is f , b) the magnitude of regional element is h^f ", are set, the regional element of magnitude of h^f corresponds to the one quantum state. When the Zustandsumme is tried to be calculated, the number of state must be known before the calculation is begun. Therefore, the property of the assembly can be generalized as the follows; namely, the Zustandsumme is

given as

$$ZC = \frac{\int \dots \int e^{-\frac{E}{kT}} dq_1 \dots dq_f dp_1 \dots dp_f}{\gamma h^f} \quad (a)$$

However, the region, $\Delta q_1 \dots \Delta q_f \Delta p_1 \dots \Delta p_f$ corresponds to $\frac{\Delta q_1 \dots \Delta q_f \Delta p_1 \dots \Delta p_f}{\gamma h^f}$ pieces of the quantum state without determination of the change γ of the equivalent atom and the equivalent atomic group. The total phase space is integrated. Then, for example to generalize this theory, the Zustandsumme of one particle in rectangular paralleopiped of each side a , b , and c , is given under unaffected external force as follows:

$$ZC = \frac{v}{h^3} (2\pi mkT)^{\frac{3}{2}} \quad (b)$$

Here, $\gamma = 1$, $f = 3$, and p_x, p_y, p_z , is momentum of direction x, y, z , respectively. On the other hand, energy Eigenvalue of this particle is given as

$$E_{n_1, n_2, n_3} = \frac{h^2}{8m} \left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2} \right) \quad (c)$$

And the number of characteristic state existed at energy range E to energy range $E + dE$ without degeneracy of

spin, and in large E is given as $\frac{4\pi v}{h^3} m \sqrt{2mE} dE$. Con-

sequently the Zustandsumme is given as $ZC = \frac{v}{h^3} (2\pi mkT)^{\frac{3}{2}}$. Then, (b) is equal to (c). Thus, the two processes of consideration can lead the same result. So, (a) is appropriate is recognized.

Next, the Zustandsumme of $A + B$ compared with the assembly A and B is given as the product form:

$$Z(A+B) = \sum_l e^{-\frac{E_{Al}}{kT}} \sum_m e^{-\frac{E_{Bm}}{kT}} = Z_A \cdot Z_C$$

Here, E_{Al} or E_{Bm} is Eigenvalue of A or B . Then, the quantity $e^{-\frac{\varphi}{\theta}} \sum_k e^{-\frac{E_k}{kT}}$ is called as Zustandsumme.

The assembly exists at the state k is given as $P_k =$

$\frac{e^{-\frac{E_k}{kT}}}{ZC}$, free energy F is given as $F = -kT \log ZC$, the

conjugate mean force to α_a is given as $\bar{\Pi}\alpha_a = kT \frac{\partial \log ZC}{\partial \alpha_a}$. The relation between thermal change of ZC and statistical mean value of energy \bar{E} with unchangeable external parameter is given as $kT^2 \frac{\partial \log ZC}{\partial T} = \bar{E} = U$.

Here, ZC is Zustandsumme of macro assembly C .

The simplification of condition is an useful thinking method to generalize the theory. Because natural change, biological reaction, biochemical reaction, or chemical reaction occurs very complicately, to treat as it is extremely difficult to solve the complicated reaction. So, to find the necessary minimum condition is one useful treatment. Such treatment may be possible to approach the ideal state. Then, the assembly that temperature is constant becomes the object of study. Also, it is canonical ensemble. So, various properties of such an assembly can be expressed by Zustandsumme. That is to say, the statistical property of the assembly existing at constant temperature can be calculated by information of Zustandsumme. Then, as the order in progress of this theory, statistical mechanical quantities must be defined by Zustandsumme of assembly existing at micro condition. Moreover, these properties of these quantities and functions must be studied to develop this theory. And using such quantities, some kinds of equilibrium and various kinds of chemical reaction must be studied. However, the discovery and the definitions of such quantities are not so easy. At the present time, this consideration is successful in progressing. Next, the four that are satisfied with such quantities or functions relating to Zustandsumme are selected and defined at this step.

Functions, \mathcal{P}^δ , $\mathcal{Q}_\sigma^\delta$, $\Theta_{\sigma(\delta)}$, and $\Theta_{\sigma(o)}$: (1) Definitions

$$\text{of four functions: } \mathcal{P}^\delta = \frac{ZC_o^\delta}{ZC_o}, \mathcal{Q}_\sigma^\delta = \frac{ZC_{\sigma(\delta)}^\delta}{ZC_{\sigma(o)}}, \Theta_{\sigma(\delta)}$$

$$= \frac{ZC_o^\delta(\delta)}{ZC_o^\delta}, \Theta_{\sigma(o)} = \frac{ZC_{\sigma(o)}}{ZC_o}$$

The four functions are defined by Zustandsumme. Here, ZC_o is Zustandsumme of assembly C_o without micro

limitation, and ZC_o^δ is Zustandsumme of assembly C_o^δ added one δ or one set of δ without change of external parameter against C_o . $ZC_{\sigma(\delta)}^\delta$ is Zustandsumme of $C_{\sigma(\delta)}^\delta$ permitted with micro limitation that fundamental state σ is a certain quantum state against the small volume as almost the equal extension as molecule, the molecular energy, or the momentum for deciding the position of the center of mass of molecule. $ZC_{\sigma(o)}$ is Zustandsumme of assembly $C_{\sigma(o)}$ with micro limitation that δ does not exist at σ certainly. One of molecule δ or each one of one set of δ exists at one fundamental state σ or at the decided one of a set of fundamental state σ . $\Theta_{\sigma(\delta)}$ is probability that δ exists at state σ in assembly C^δ . $\Theta_{\sigma(o)}$ is probability that δ does not exist at state σ . (2) Expansion of definition: the defined functions show the coefficient of Zustandsumme increment by individual procedure. \mathcal{P}^δ is the coefficient of Zustandsumme increment of assembly C_o^δ that δ of component exists more than assembly C_o without micro limitation. $\mathcal{Q}_\sigma^\delta$ is the coefficient of Zustandsumme increment that δ is added to the vacant space σ of $C_{\sigma(o)}$ from the outside. $\Theta_{\sigma(\delta)}$ or $\Theta_{\sigma(o)}$ is the probability that without micro limitation δ exists certainly at the decided state σ in the assembly C_o^δ , or does not exist at the decided state σ in C_o respectively. Those relations can be expressed as formulas:

$$\log \mathcal{P}^\delta = \Delta p_\delta \log ZC_o, \log \mathcal{Q}_\sigma^\delta = \Delta q_{\sigma(\delta)} \log ZC_{\sigma(o)},$$

$$\log \Theta_{\sigma(\delta)} = \Delta \theta_{\sigma(\delta)} \log ZC_o^\delta, \log \Theta_{\sigma(o)} = \Delta \theta_{\sigma(o)} \log ZC_o$$

So, λ expresses \mathcal{P}^δ , $\mathcal{Q}_\sigma^\delta$, $\Theta_{\sigma(\delta)}$, $\Theta_{\sigma(o)}$, and $\Delta_\lambda \log ZC$ is increment of $\log ZC$ dependend upon suitable procedure related to λ . Its procedure must be accessible to the assembly C . This limitation is important to have the physical meaning. As the procedure that δ does not exist certainly at state σ of assembly C_o without micro limitation can be operated, $\Theta_{\sigma(o)}$ can have the physical meaning. Next, the two kinds of increment are tried to be considered. Δ expresses the primary increment. The two arbitrary quantities of these Δ are expressed by Δ_1 and Δ_2 . And, secondary increments are expressed respectively as $\Delta_1 \Delta_2 \log ZC \equiv \Delta_1 \log ZC (\Delta_2) - \Delta_1 \log ZC$ and $\Delta_1 \Delta_2 P \equiv \Delta_1 P (\Delta_2) - \Delta_1 P$. $\Delta_\lambda P$ expresses increment of property P produced by the behavior that the procedure related to λ is operated to assembly.

$\Delta p_\lambda \log ZC$ expresses increment of $\log ZC$ produced by increasing of quantity $\Delta_\lambda P$ against P without λ . $C(\Delta_2)$ is assembly produced by operating procedure related to Δ_2 against C . $P(\Delta_2)$ is the value obtained by operating procedure Δ_2 against P . Thus, as these definitions are decided, higher order increment over tertiary can be defined similarly. This decision method defined first increment at the first step. So, at the second step, the secondary increment can be defined. Moreover, at the third step, the tertiary increment can be defined. Thus, this new theoretical treatment performs the establishment of consideration according to the process of step by step. Namely, the related condition that is added from the ideal state to the practical, complicated state step by step develops this theory for the generalized theory. (3) Approximation of definition: the fundamental state σ_1 and σ_2 are decided by the two procedures like $\Delta_1 \equiv \Delta_{\theta, \sigma_1}(\delta)$ and $\Delta_2 \equiv \Delta_{\theta_2, \sigma_2}(\delta)$. And intermolecular direct interaction exists in each one. Then, neglect the secondary increment against the first increment except the two cases described above. Of course, increment over secondary can be neglected when the fundamental state cannot be decided like one or both of procedure is $\Delta p\delta$.

$$i) \Delta p_2 (\log ZC_0 + \Delta p\delta_1 \log ZC_0) = \Delta p_2 \log ZC_0$$

$$\log ZC_0 + \Delta p\delta_1 \log ZC_0 = \log ZC_0^{\delta_1}$$

Then,

$$\frac{ZC_0^{\delta_1 + \delta_2}}{ZC_0^{\delta_1}} = \frac{ZC_0^{\delta}}{ZC_0}$$

and

$$iP^{\delta_1 + \delta_2} = \frac{ZC_0^{\delta_1 + \delta_2}}{ZC_0^{\delta_1}} \frac{ZC_0^{\delta_1}}{ZC_0}$$

Therefore, $iP^{\delta_1 + \delta_2} = iP^{\delta_1} iP^{\delta_2}$. Also, $\delta = \sum_g \nu_g \delta_g$.

Here, δ is composed with $\nu_1, \nu_2, \dots, \nu_g, \dots$ pieces of $\delta_1, \dots, \delta_g, \dots$ kinds of molecule. Similarly, $iP^\delta = \prod (iP^{\delta_g})^{\nu_g}$.

ii) Similarly to the above description,

$$\Delta_{\sigma\theta}(\delta) (\log ZC_0 + \Delta p\delta \log ZC_0) = \Delta_{\sigma}(\delta) \log ZC$$

consequently,

$$\Delta_{\theta\sigma}(\delta) \log ZC_0^\delta = \Delta_{\theta\sigma}(\delta) \log ZC_0$$

Therefore,

$$\Theta_{\sigma}(\delta) = \frac{ZC_{\sigma}(\delta)}{ZC_0}$$

iii) Arbitrary increment of $\log ZC$ is given as

$$\Delta_\lambda \log ZC = (\Delta_\lambda \log ZC)_P + \sum_j \Delta p_{\lambda j} \log ZC.$$

$(\Delta_\lambda \log ZC)_P$ is increment in the case that all objective property P_j is unchangeable. And, $\Delta p_{\lambda j} \log ZC$ is expanded to the power series of $\Delta_\lambda P_j$ and the term over secondary is neglected.

$$\Delta p_{\lambda j} \log ZC = \frac{\partial \log ZC}{\partial P_j} \Delta_\lambda P_j$$

Consequently,

$$\Delta_\lambda \log ZC = (\Delta_\lambda \log ZC)_P + \sum_j \frac{\partial \log ZC}{\partial P_j} \Delta_\lambda P_j$$

Such approximation of function is valuable to develop this new theoretical treatment.

The correlation to $iP^\delta, \mathbf{q}_\sigma^\delta, \Theta_{\sigma}(\delta), \Theta_{\sigma}(\sigma)$:

$$\mathbf{q}_\sigma^\delta = \frac{\Theta_{\sigma}(\delta)}{\Theta_{\sigma}(\sigma)} iP^\delta$$

is directly from the above described

relations.

$$iP^\delta = \Theta_{\sigma}(\sigma) \frac{\mathbf{q}_\sigma^\delta / |\sigma|}{\Theta_{\sigma}(\delta) / |\sigma|}$$

The relation can be re-

written. However, δ is composed with only one molecule, σ is almost the same magnitude of vacant space against molecule that decides the position of the center of mass of δ . $|\sigma|$ is volume of vacant space σ .

And, when $|\sigma|$ approaches to 0, $ZC_{\sigma}(\sigma)$ becomes equal to ZC_0 . Consequently, $\Theta_{\sigma}(\sigma)$ becomes 1. $\Theta_{\sigma}(\delta) / |\sigma|$ is the ratio of the probability that the center of mass of the molecule is in the vacant space σ to the volume of the vacant space. When $|\sigma|$ approaches to 0, if N^δ expresses the concentration of δ at astrigent point, $N^\delta =$

$$\lim_{|\sigma| \rightarrow 0} \frac{\Theta_{\sigma}(\delta)}{|\sigma|}$$

is obtained.

Therefore, if it is defined that iP^δ is independent on the volume $|\sigma|$ of vacant space as $|\sigma|$ approaches to 0, $\mathbf{q}_\sigma^\delta / |\sigma|$ approaches to one constant value with $\Theta_{\sigma}(\delta) / |\sigma|$. If Q^δ expresses the extremal value of $\mathbf{q}_\sigma^\delta / |\sigma|$, namely, if

$$Q^\delta = \lim_{|\sigma| \rightarrow 0} \frac{\mathbf{q}_\sigma^\delta}{|\sigma|}$$

is given, $iP^\delta = \frac{Q^\delta}{N^\delta}$ is obtained.

The relation among four functions is studied and is defined in this way. So, the relation is valuable to develop

this theoretical treatment for chemical reaction. Such fundamental consideration is successful to analyze the chemical reaction on the basic point.

Summary

The relation to quantum mechanics and thermodynamics is considered by this new fundamental theoretical treatment. The quantity H led by statistical mechanics and the other quantities related to it are considered with any quantity in thermodynamics. The approximate and probable behavior of the assembly composed with a number of chemical species are taken up as one object. It is natural that the method of statistical mechanics are applied. The following conditions are assumed as a fundamental limitation: (1) the macro assembly is canonical ensemble, (2) the assembly exists at thermodynamical equilibrium. So, the probability against taking Eigenvalue of energy of the assembly in the ensemble is considered with the external and internal parameters. The quantity H in the canonical ensemble is affected by the distribution coefficient and the both parameters under the condition of slight change. So, the change of the quantity is considered. While the assembly existing at thermodynamical equilibrium is made to change slightly, the entropy change is considered with the both parameters. The quantity of thermodynamics is considered with the quantity of statistical mechanics.

Now, the classical approximation of Zustandsumme is considered in the case that the number of state is known. In the phase space of the assembly had the decided degree of freedom, a certain magnitude of regional element corresponds to one of quantum state. Also, the Zustandsumme of one particle in a rectangular parallelepiped, the energy of the system expressed by mass and momentum in x , y , and z directions, the Zustandsumme expressed in relation of quantum state, the Zustandsumme obtained in relation to the number of characteristic state without degeneracy by spin and the undecidedness of the Eigenvalue of the particle are considered respectively and correlatively. The equal value of the Zustandsumme can be calculated by two different methods to prove the appropriation of the

procedure. The sum of the independent mechanical Zustandsumme is expressed by the product of the two parts of Zustandsumme. The Zustandsumme of the macro assembly is considered with the probability of existence at the state. The relation of the free energy against the Zustandsumme is considered like in the case of the conjugate mean force against the Zustandsumme. And the temperature change of the Zustandsumme can be related to statistical mean value of energy. The Zustandsumme is expressed in those relations.

Next, four functions, \mathcal{P}^δ , \mathbf{q}_σ^δ , $\Theta_{\sigma(\delta)}$, and $\Theta_{\sigma(o)}$, given by the representative ratio of Zustandsumme are defined at first on the base of this new theoretical treatment. And, the expansion of definition is tried successively. These functions give a coefficient of increment of Zustandsumme respectively and are expressed by one formula, $\log \lambda = \Delta_\lambda \log ZC$. So, the increment of the secondary is defined similarly to the definition of increment of the first. This procedure can be applied to tertiary and over it. Of course, the approximation had to be considered. The assumptions: a) there is no direct interaction in molecule, b) the increment of secondary and over are neglected to first. So, the following relations are obtained: i) $\mathcal{P}^{\delta_1 + \delta_2} = \mathcal{P}^{\delta_1} \mathcal{P}^{\delta_2}$, $\mathcal{P}^\delta =$

$$\frac{g}{\Pi(\mathcal{P}^\delta)^{\nu g}} \nu g, \text{ ii) } \Theta_{\sigma(\delta)} = \frac{ZC\delta(\delta)}{ZC_0}, \text{ iii) } \Delta_\lambda \log ZC =$$

$$(\Delta_\lambda \log ZC)_P + \sum_j \frac{\partial \log ZC}{\partial P_j} \Delta_\lambda P_j. \text{ Next, the correlation}$$

of functions, $\mathbf{q}_\sigma^\delta = \frac{\Theta_{\sigma(\delta)}}{\Theta_{\sigma(o)}} \mathcal{P}^\delta$ is obtained. Moreover,

$$\mathcal{P}^\delta = \Theta_{\sigma(o)} \frac{\mathbf{q}_\sigma^\delta / |\sigma|}{\Theta_{\sigma(\delta)} / |\sigma|}, \mathcal{N}^\delta = \lim_{|\sigma| \rightarrow 0} \frac{\Theta_{\sigma(\delta)}}{|\sigma|}, Q^\delta = \lim_{|\sigma| \rightarrow 0} \frac{\mathbf{q}_\sigma^\delta}{|\sigma|}, \text{ and } \mathcal{P}^\delta = \frac{Q^\delta}{\mathcal{N}^\delta} \text{ are obtained. Here, } \delta \text{ is}$$

composed with only one molecule, $|\sigma|$ is the volume of vacant space, \mathcal{N}^δ is concentration of δ at the astringent point, and Q^δ is the extremal value of $\mathbf{q}_\sigma^\delta / |\sigma|$.

References

- 1) J. W. Gibbs; Elementary Principles in Statistical Mechanics, Yale Univ. Press. 1902, New Haven.
- 2) P. Ehrenfest, T. Ehrenfest; Encykl. d. Math. Wiss., IV 2 ii, Helt 6.
- 3) L. Pauling, E. B. Wilson; Introduction to Quantum Mechanics, McGRAW-HILL, 1935, New York.
- 4) H. Eyring; J. Chem. Phys., 3 (1935)
- 5) M. G. Evans & M. Polanyi; Trans. Faraday Soc., 31 (1935)
- 6) R. C. Tolman; The Principles of Statistical Mechanics, Oxford Univ. Press., 1938, Glasgow
- 7) R. C. Tolman; The Principles of Statistical Mechanics, Oxford, 290 (1938), Glasgow
- 8) J. E. Mayer; Statistical Mechanics; John Wiley & Sons, 1940, New York
- 9) A. I. Khinchin; Mathematical Foundations of Statistical Mechanics, Dover Pub., 1949, New York
- 10) H. Goldstein; Classical Mechanics, Addison-Wesley Pub., 1950, London
- 11) F. W. Sears; Thermodynamics, the Kinetic Theory of Gases, and Statistical Mechanics, Addison-Wesley Pub., 1953, Massachusetts
- 12) L. I. Schiff; Quantum Mechanics, 3rd Ed. Inter. Stu. Ed., 1955, New York
- 13) P. A. M. Dirac; The Principles of Quantum Mechanics, 4th Ed., Oxford Clarendon Press., 1958, Glasgow
- 14) F. W. Sears; Thermodynamics, Addison-Wesley Pub., 1959, Massachusetts
- 15) A. A. Frost, R. G. Pearson; Kinetics and Mechanism, John Wiley & Sons, 1961, New York
- 16) E. Schrödinger; Statistical Thermodynamics, Cambridge Univ. Press., 1964, Cambridge
- 17) R. P. Feynman, A. R. Hibbs; Quantum Mechanics and Path Integrals, McGRAW-HILL, 1965, New York
- 18) T. C. Bradbury; Theoretical Mechanics, Wiley Inter. Ed., 1968, New York
- 19) W. Miller, H. F. Schasfer, B. J. Berne, G. A. Segal; Modern Theoretical Chemistry, A. B. Penum Press., 1977, New York
- 20) D. R. Cox, P. A. W. Lewis; The Statistical Analysis of Series of Events, Chapman & Hall, 1978, London
- 21) B. H. Lavenda; Thermodynamics of Irreversible Processes, Macmillan, 1978, London
- 22) K. Baclawski, M. D. Donsker; Mark Kac: Probability, Number Theory, and Statistical Physics, Selected Papers, MIT Press., 1979, Cambridge
- 23) K. Horitsu; Bull. Tokyo Kasei Daigaku, 23(2) 15 (1983)
- 24) K. Horitsu; *ibid.*, 23(2) 23 (1983)
- 25) K. Horitsu; *ibid.*, 24(2) 23 (1984)
- 26) K. Horitsu; *ibid.*, 24(2) 35 (1984)

化学反応の理論的取扱

第5報 量子統計力学と熱力学との関係

堀津圭佑

(昭和59年9月29日受理)

量子力学と熱力学の関係をこの新理論的取扱で考察した。統計力学の量 H と関係ある他の量を熱力学の量と考察し、化学種の集団の近似的確率的行動を目的とし、統計力学を応用した。基本制限として(1)巨視的集団は正準集合(2)集団は温度平衡にある。集合中の集団のエネルギー固有値をとる確率を内部と外部パラメーターと考察し、正準集合の H は小変化条件下で分布係数と両パラメーターに影響され、熱力学的平衡下の集団を僅少変化させ、エントロピー変化と両パラメーターを考察し、熱力学の量と統計力学の量を考察した。

さて状態和の古典的近似を状態数既知の場合に考察し、決定自由度の集団内の位相空間で領域のある大きさは1量子状態に対応する。また直方体中の1粒子の状態和、 x , y , z 方向に質量と運動量で表わされた系のエネルギー、量子状態と関係の状態和、スピンによる縮退なしの固有状態数に關係の状態和、粒子の固有値の未決定を個別的關連的に考察した。操作の妥当性を証明するため状態和の等価を2相異法で計算ができた。無關係な力学的状態和は2個の状態和の積で表わされ、巨視的集団の状態和は状態に存在する確率で考察し、自由エネルギーと状態和の關係は状態和と共役平均力と同様に考察し、状態和の温度変化はエネルギーの統計的平均値と關係付けられた。

次に新理論的取扱の基礎とし4関数を状態和の基礎として定義し、定義の拡張を試み成功した。これらの関数は状態和の増加をそれぞれ与え、式 $\log \lambda = \Delta_\lambda \log ZC$ で表示し、二次増加を一次増加の定義に従い定義し、この操作を三次と三次以上に試みた。勿論近似は考察済である。仮説 a) 分子間の直接相互作用はない b) 二次とそれ以上の増加は一次に対し無視した。そして

$$i) P^{\delta_1 + \delta_2}, P^\delta = \prod (P^{\delta g})^g \quad ii) \mathbb{H}_{\sigma(\delta)} = \frac{ZC_{\sigma(\delta)}}{ZC_0} \quad iii) \Delta_\lambda \log ZC \quad \text{相互關係} \quad q_\sigma^\delta = \frac{\mathbb{H}_{\sigma(\delta)}}{\mathbb{H}_{\sigma(0)}} P^\delta,$$

$$P^\delta = \mathbb{H}_{\sigma(0)} \frac{q_\sigma^\delta / |\sigma|}{\mathbb{H}_{\sigma(\delta)} / |\sigma|}, \quad N^\delta = \lim_{|\sigma| \rightarrow 0} \frac{\mathbb{H}_{\sigma(\delta)}}{|\sigma|}, \quad Q^\delta = \lim_{|\sigma| \rightarrow 0} \frac{q_\sigma^\delta}{|\sigma|}, \quad P^\delta = \frac{Q^\delta}{N^\delta} \quad \text{をえた.}$$