

One Theoretical Treatment of Chemical Reaction

Part 6 Relation to Quantum Statistical Mechanics and Thermodynamics Partially

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Introduction

One part of basic consideration of this new theoretical treatment to chemical reaction is described relating to connection with quantum statistical mechanics and thermodynamics. Moreover, the definition and the theory that are important to expand this new theoretical-treatment can be recognized after various considerations were tried for them.

Several functions in thermodynamics are considered. At first, the relation between free energy of Helmholtz, internal energy in thermodynamics and Zustandsumme is considered as one example. Also, as the relation between statistical mechanics and thermodynamics was discussed in the previous papers^{20~24)}, these considerations could be applied very effectively. And chemical potential in thermodynamics is equal to reversible work per mole is led. According to Lewis,²⁾ partial molar free energy, partial molar internal energy, and partial molar entropy are obtained. And chemical potential of material added later is not changed by any material added before, when extreme slight material, $\delta_1, \dots, \delta_g, \dots$, are added into a large system.

Force, work, and energy are considered in regard to Zustandsumme. The work that the assembly shifts from state I to state II holding to exist at statistical equilibrium is reversible work. So, the definition and the theory of λ of the assembly that is unchanged are considered. And the relation between four functions, μ^δ , q_σ^δ , $\Theta_{\sigma(\delta)}$, and $\Theta_{\sigma(o)}$, defined by ratio of Zustandsumme and reversible work is considered. $-RT \log \lambda = \Delta_\lambda(-kT \log ZC)$. $\Delta_\lambda = \Delta_\lambda \cdot N_A$.

The relative equation of μ^δ at equilibrium is con-

$$\text{sidered. } \frac{a}{\prod (\mu^\delta a)^{\nu_a^A}} = \frac{b}{\prod (\mu^\delta b)^{\nu_b^B}} = \dots$$

λ for the assembly holding the variable external parameter is considered. λ defined in the above described section is related to the assembly that external parameter holds constant. Now, the definition and the theory of λ are expanded to the assembly that external parameter does not be held always constant. However, procedure λ is added in the assembly A that is related to other assembly K according to the following three conditions. (i) External parameter held extensive property, volume or surface area etc., changes in regard to each one of A and K . But the sum of it, β_b , belonging to A or K is unchangeable. Also, external parameter except such kind is unchangeable to each one of A and K . (ii) There is not the conjugate force against β_b that acts on $A+K$ from the outside. (iii) After the value of β_b is decided, energy state of each assembly is decided independently, mechanically, mutually. Now, the energy state of each gaseous part is decided by the volume of A that is only one external parameter of part A . The assembly $A+K$ is one special case of the assembly treated in the above described sections, "several functions in thermodynamics", "force, work, and energy". Of course, the definition and the theory are valid to $A+K$.

Equivalence of λ between assembly $A+K$ and A_β is considered. $\log \lambda = \Delta_\lambda \log Z(A+K) = (\Delta_\lambda \log Z(A+K)) +$

$$\sum_b \frac{\partial \log Z(A+B)}{\partial \beta_b} \Delta_\lambda \beta_b$$

$$(\Delta_\lambda \log Z(A+K))_\beta = \Delta_\lambda \log Z A_\beta + (\Delta_\lambda \log ZK)_\beta$$

therefore, $\log \lambda = \Delta_\lambda \log Z(A+K) = \Delta_\lambda \log Z A_\beta$

The values of two λ s defined in the above description

are equal to each one.

Development formula of λ concerning A and the quantity led from it are considered.

$-kT \log Z(A+K)$ is developed to the form related to assembly A .

Also, $\bar{\pi}_{\beta_b}^A + \bar{\pi}_{\beta_b}^K = 0$ is valid. And $\log Z(A+K)$ can be expressed with only variable of A . Next, thermal change of $Z(A+K)$ is considered and two expressions of this relation can be obtained. Also, thermal change of λ is considered and is obtained as (a). Moreover, thermal change of λ defined in regard to assembly A_β is considered and is obtained as (b). In comparison between

(a) : $kT^2 \frac{\partial \log \lambda}{\partial T}$ and (b) : $kT^2 \left(\frac{\partial \log \lambda}{\partial T} \right)_\beta$, each value of λ defined in regard to the two assemblies is equal. However, thermal change is unequal generally.

As this part is belonged to Introduction, moreover, though expressions by these equations are useful practical and understandable especially, many related equations are omitted to avoid duplication. Refer to the section, Gedanken experiment.

This new theoretical treatment is studied for generalization of the theory and definition in chemical reaction as one object.

The referred publications^{1~24)} are very effective to develop this new theoretical treatment of chemical reaction.

Experimental and Results, Gedanken Experiment

Several functions in thermodynamics: the free energy of Helmholtz F and the internal energy U in thermodynamics are given by the following equations, eq. (VI - 1) and eq. (VI - 2), respectively as shown in the previous paper²⁴⁾.

$$F = -kT \log ZC \quad (VI - 1)$$

$$U = kT^2 \frac{\partial \log ZC}{\partial T} \quad (VI - 2)$$

Here, T is thermodynamic temperature. And ZC is the Zustandsumme of the macro assembly.

The following relations are obtained from the both equations, eq. (VI - 1) and eq. (VI - 2), directly as

shown in the following equation, eq. (VI - 3).

$$U = F - T \frac{\partial F}{\partial T} \quad (VI - 3)$$

And, from the following equations, eq. (VI - 4), shown in the previous paper⁵⁾ and eq. (VI - 1), the following relation shown in the following equation, eq. (VI - 5), is obtained.

$$\frac{\delta \varphi}{\theta} + \frac{1}{\theta} \sum_a \bar{\pi}_{\alpha_a} \delta \alpha_a - \frac{\varphi - \bar{E}}{\theta^2} \delta \theta = 0 \quad (VI - 4)$$

$$-\bar{\pi}_{\alpha_a} = \frac{\partial F}{\partial \alpha_a} \quad (VI - 5)$$

Also, the following relation shown in the following equation, eq. (VI - 7), is obtained from the following relation shown in the following equation, eq. (VI - 6)²⁴⁾, which may be explained in the next section.

$$-RT \log \lambda = \Delta_\lambda (-kT \log ZC) \quad (VI - 6)$$

Here, λ is P^δ , q_σ^δ , $\Theta_{\sigma(\delta)}$, or $\Theta_{\sigma(o)}$ as shown in the previous paper²⁴⁾.

Δ_λ is a product of Avogadro's number N_A and the increment Δ_λ .

$$\Delta_\lambda F = -RT \log \lambda \quad (VI - 7)$$

Next, the following relation shown in the following equation, eq. (VI - 9), is obtained from the following relation shown in the following equation, eq. (VI - 8), that may be explained in the next section.

$$RT^2 \frac{\partial \log \lambda}{\partial T} = \Delta_\lambda \bar{E} \quad (VI - 8)$$

$$\Delta_\lambda U = RT^2 \frac{\partial \log \lambda}{\partial T} \quad (VI - 9)$$

Or the relation shown in the following equation, eq. (VI - 10), is obtained from eq. (VI - 3).

$$\Delta_\lambda U = \Delta_\lambda F - T \frac{\partial \Delta_\lambda F}{\partial T} \quad (VI - 10)$$

Moreover, from the relation in the both following equations, eq. (VI - 11) and eq. (VI - 12), shown in the previous paper²⁴⁾, the following equations, eq. (VI - 13), eq. (VI - 14), and eq. (VI - 15), are obtained.

$$H = \frac{\varphi - \bar{E}}{\theta} \quad (\text{VI} - 11)$$

$$S = -kH \quad (\text{VI} - 12)$$

$$-S = kH = \frac{\varphi - \bar{E}}{T} = \frac{F - U}{T} \quad (\text{VI} - 13)$$

$$\text{or } F = U - TS \quad (\text{VI} - 14)$$

Consequently,

$$\Delta_\lambda F = \Delta_\lambda U - T \Delta_\lambda S \quad (\text{VI} - 15)$$

Then, from eq. (VI - 3) and eq. (VI - 14), the both following relations are obtained as shown in the following equations, eq. (VI - 16) and eq. (VI - 17).

$$S = -\frac{\partial F}{\partial T} \quad (\text{VI} - 16)$$

$$\Delta_\lambda S = -\frac{\partial \Delta_\lambda F}{\partial T} \quad (\text{VI} - 17)$$

Especially, in the case that λ is equal to P^δ , $\lambda = P^\delta$, it is regarded as follows; the reversible work per mole of δ , $-RT \log P^\delta$, which requires to work from $C_0 + \delta$ to C_0^δ is the same as the chemical potential μ^δ . Namely, this relation is expressed as the following equation, eq. (VI - 18).

$$\mu^\delta = -RT \log P^\delta \quad (\text{VI} - 18)$$

Therefore, in this case, the following equations, eq. (VI - 7), eq. (VI - 9), eq. (VI - 10), eq. (VI - 14), and eq. (VI - 17), are expressed as shown in the following equations, eq. (V - 19). eq. (VI - 20), eq. (VI - 21), eq. (VI - 22), and eq. (VI - 23), respectively.

$$\mu^\delta = \bar{F}^\delta \quad (\text{VI} - 19)$$

$$RT^2 \frac{\partial \log P^\delta}{\partial T} = \bar{U}^\delta \quad (\text{VI} - 20)$$

$$\mu^\delta = \bar{U}^\delta + T \frac{\partial \mu^\delta}{\partial T} \quad (\text{VI} - 21)$$

$$\mu^\delta = \bar{U}^\delta - T \bar{S}^\delta \quad (\text{VI} - 22)$$

$$\bar{S}^\delta = -\frac{\partial \mu^\delta}{\partial T} \quad (\text{VI} - 23)$$

Here, \bar{F}^δ , \bar{U}^δ , and \bar{S}^δ show $\Delta_{P^\delta} F$, $\Delta_{P^\delta} U$, and $\Delta_{P^\delta} S$ respectively. And they are called as partial molar free energy, partial molar internal energy, and partial molar entropy respectively according to G. N. Lewis²⁾.

In consequence, the relation by the following equation, eq. (VI - 24), that was explained in the previous paper²⁴⁾ can be written as the following equation, eq. (VI - 25).

$$P^\delta = \prod_g (P^\delta g)^{\nu_g} \quad (\text{VI} - 24)$$

$$\mu^\delta = \sum_g \nu_g \mu^\delta g \quad (\text{IV} - 25)$$

The meaning of this equation, eq. (VI - 25), shows the point that the chemical potential of the material added later is not changed by the any material added before, in the case that the extreme slight material, $\delta_1, \dots, \delta_g, \dots$, are added into a large material system. It is regarded as a self-evident truth in thermodynamics.

Force, work, and energy: while the assembly is kept to exist at statistical equilibrium commonly, and when a set of internal and external parameters can be changed independently and continuously with each other, the following relation shown in the following equation, eq. (VI - 27), is obtained by the following equation, eq. (VI - 26), shown in the previous paper²⁴⁾.

$$\bar{\Pi}_{\alpha_a} = kT \frac{\partial \log ZC}{\partial \alpha_a} \quad (\text{VI} - 26)$$

Here, $\bar{\Pi}_{\alpha_a}$ is conjugate mean force of α_a .

$$-kT \frac{\partial \log ZC}{\partial \alpha_a} = -\bar{\Pi}_{\alpha_a} \quad (\text{VI} - 27)$$

Therefore, the following relation is obtained as shown in the following equation, eq. (VI - 28):

$$-kT \log \frac{ZC_{II}}{ZC_I} = \sum_a \int_{\alpha_a(I)}^{\alpha_a(II)} (-\bar{\Pi}_{\alpha_a} d\alpha_a) \quad (\text{VI} - 28)$$

Here, ZC_I and ZC_{II} are the Zustandsumme of the assembly C when a set of parameter shows $\alpha_a(I)$ and $\alpha_a(II)$ respectively. The right side of eq. (VI - 28) is the work that requires to shift from state I to state II, while the assembly is kept to exist at statistical equilibrium. And the work is called as reversible work.

The external parameter of the assembly $C_0 + \delta$ that is composed with the independent molecule δ is not changed. However, the assembly C_0^δ is made mutually by the independent change of the internal parameter at the distance that is enough far from the macro assembly C_0 . Now, in $C_0 + \delta$, $Z(C_0 + \delta)$ is equal to $ZC_0Z\delta$, $Z(C_0 + \delta) = ZC_0Z\delta$, as C_0 is independent from δ mutually. Therefore, the relation, $ZC_{II}/ZC_I = ZC_0^\delta/ZC_0$, is obtained when the standard state is selected as $Z\delta$ becomes 1, $Z\delta = 1$. Namely, when C_I is equal to $C_0 + \delta$, $C_I = C_0 + \delta$, and C_{II} is equal to C_0^δ , $C_{II} = C_0^\delta$, the left side of eq. (VI - 28) becomes $-kT \log p^\delta$. That is, it is equal to the corresponding reversible work to the right side of the equation. Similarly, $-kT \log q_\sigma^\delta$ is the work that requires to shift δ from the standard state to the state σ without the change of external parameter of $C_0(\sigma)$. But, the state σ is one that the assembly $C_0(\sigma)$ is vacant beforehand. And $-kT \log \Theta_{\sigma(\delta)}$ or $-kT \log \Theta_{\sigma(o)}$ is the reversible work that is necessary to add the limitation to the assembly C_0 without the change of external parameter. The limitation includes the importance that δ exists certainly at the state σ or not. As the other three reversible works except $-kT \log p^\delta$ have the micro property, of course, it does not correspond to any thermodynamical function that was defined already.

These reversible works, $-kT \log p^\delta$, $-kT \log q_\sigma^\delta$, $-kT \log \Theta_{\sigma(\delta)}$, and $-kT \log \Theta_{\sigma(o)}$ are possible to be rewritten summarily as shown in the following equations, eq. (VI - 30) and eq. (VI - 31) according to the following equation, eq. (VI - 29), in the previous paper²⁴.

$$\log \lambda = \Delta_\lambda \log ZC \quad (\text{VI} - 29)$$

Here, λ is p^δ , q_σ^δ , $\Theta_{\sigma(\delta)}$, or $\Theta_{\sigma(o)}$. And $\Delta_\lambda \log ZC$ is the increment of $\log ZC$ by the appropriate procedure related to λ .

$$-kT \log \lambda = \Delta_\lambda (-kT \log ZC) \quad (\text{VI} - 30)$$

Or

$$-RT \log \lambda = \Delta_\lambda (-kT \log ZC) \quad (\text{VI} - 31)$$

Here, Δ_λ is the quantity that the increment Δ_λ is multi-

plied by Avogadro's number N_A .

When the external parameter is unchangeable, the thermal change of ZC is expressed as shown in the following equation, eq. (VI - 33), according to the following equation, eq. (VI - 32), shown in the previous paper²⁴.

$$kT^2 \frac{\partial \log ZC}{\partial T} = \frac{\sum E_k e^{-\frac{E_k}{kT}}}{\sum e^{-\frac{E_k}{kT}}} = \bar{E} = U \quad (\text{VI} - 32)$$

$$kT^2 \frac{\partial \log ZC}{\partial T} = \bar{E} \quad (\text{VI} - 33)$$

Therefore, the thermal change of λ is expressed as the following equation, eq. (VI - 34) from eq. (VI - 31).

$$RT^2 \frac{\partial \log \lambda}{\partial T} = \Delta_\lambda \bar{E} \quad (\text{VI} - 34)$$

Relative equation of p^δ at equilibrium: when the component δ of the assembly C^δ can shift during various states, $\delta^A, \delta^B, \dots$, enough rapidly within the objective time, $ZC^{\delta A}, ZC^{\delta B}, \dots$ became the same value. Because, if the assembly exists at any state, this subject does not come into question against the Zustandsumme. The Zustandsumme is sum of Boltzmann's factor related to all possible state of the assembly. Consequently, from the following equation, eq. (VI - 35) related to the definition of p^δ , the following relation is obtained as shown in the following equation, eq. (VI - 36):

$$p^\delta = \frac{ZC_0^\delta}{ZC_0} \quad (\text{VI} - 35)$$

Here, ZC_0 is the Zustandsumme of the assembly C_0 that is not permitted by the micro limitation. And ZC_0^δ is the Zustandsumme of the assembly C_0^δ that is obtained by the addition of one piece of molecule δ or a set of molecule δ into the assembly C_0 without the change of external parameter.

$$p^\delta \delta^A = p^\delta \delta^B \quad (\text{VI} - 36)$$

The states of $\delta, \delta^A, \delta^B, \dots$, that satisfies eq. (VI - 36) exist at equilibrium mutually.

If $\delta^A, \delta^B, \dots$ are composed with ν_a^A, ν_b^B, \dots , pieces of molecule, $\delta_a^A, \delta_b^B, \dots$ respectively, according to eq. (VI - 36) and eq. (VI - 37) shown in the previous paper²⁴, the following relation as shown in the following equation, eq. (VI - 39), is obtained from the following equation, eq. (VI - 38).

$$p^\delta = \frac{g}{\Pi} (p^\delta g)^{\nu g} \quad (\text{VI} - 37)$$

$$\delta^A = \sum_a \nu_a^A \delta_a^A, \quad \delta^B = \sum_b \nu_b^B \delta_b^B, \dots \quad (\text{VI} - 38)$$

$$\frac{a}{\Pi} (p^\delta \delta_a^A)^{\nu_a^A} = \frac{b}{\Pi} (p^\delta \delta_b^B)^{\nu_b^B} = \dots \quad (\text{VI} - 39)$$

Here, δ^A and δ^B must be composed with the same element, but the molecule that composes them is possible to be different.

λ for the assembly held the variable external parameter: the all λ defined in the above description is related to the assembly that the external parameter is kept constant in the procedure connected with it. In this section, consider to expand the definition and the theory of λ to the case that the external parameter of the objective assembly is not always kept constant. At first, consider the case that the procedure λ is added into the assembly A alone. However, the assembly A is related to the other assembly K according to the following conditions. Namely, (i) the external parameter holding the extensive property as such volume, surface area etc. is changeable to A and K respectively. However, the sum of the external parameter β_b of A and the external parameter of K is unchangeable. Also, the other kind of external parameter is unchangeable to each one of the assembly A and K . (ii) There is no conjugate force to β_b that acts on $A+K$ from the outside. (iii) After the value of β_b is decided, the state of energy of each assembly is decided independently, mechanically, mutually, and respectively.

As a simple example that satisfies such a condition, the assembly that is composed with two separated gaseous parts of A and K is possible to be considered. The two gaseous parts are separated by the piston that can move freely in a cylinder without leakage. Namely, it is regarded that the state of energy of each gaseous part is decided by the volume of A in this case. And the volume of A is only one external parameter of part A .

However, the conjugate force to parameter does not act from the outside.

In this case, the assembly $A+K$ is the special case of the assembly treated in the above described section, as the external parameter is unchangeable. Of course, the definition and the theory described in the above section are valid to the $A+K$. Also, in the case that β_b is unchangeable, the definition and the theory are valid to only the assembly A similarly. Then, such an assembly A is expressed as A_β . In this way, as the assembly C of eq. (VI - 29), λ is possible to be defined by the selection of either of the two, $A+K$ or A_β in regard to the assembly $A+K$ or A_β . The former is called as λ of the assembly A holding a variable external parameter or is called as λ of $A+K$ simply. On the other hand, the later is called as λ of A_β .

While the several equations that may be obtained in the following sections are compared with λ of A_β , try to express them using the function of thermodynamics.

Equivalence between λ of the assembly $A+K$ and λ of the assembly A_β : the property of the assembly is considered slightly partially at first. But, the detailed description is shown in the previous papers^{20~23}. As one part of the description, the chance that the specific elementary reaction occurs at a certain time, and the property of the elementary reaction are given by calculating the statistical mean of the region, after the region, which corresponds to the same chemical composition as the chemical composition of the objective assembly at the time, is cut off from the canonical ensemble. However, it is assumed that the canonical distribution is held in this region only, as shown in the contents of the section of thermal equilibrium. Especially, the part that the Zustandsumme corresponds is called as the Zustandsumme of the assembly. So, λ is defined by usage of Zustandsumme like the case of complete equilibrium. And, if the point that the assembly is composed with constant chemical composition is regarded as micro limitation, all various theories in regard to λ expanded in the above described sections are possible to be applied to the assembly that exists at thermal equilibrium.

Next, it is considered as follows; the value of λ that is defined by the two methods is equal to each other. Ac-

ording to the following equation, eq. (VI - 40), shown in the previous paper²⁴⁾ the following relation as shown in the following equation, eq. (VI - 41), is obtained.

$$\Delta_\lambda \log ZC = (\Delta_\lambda \log ZC)_P + \sum_j \frac{\partial \log ZC}{\partial P_j} \Delta_\lambda P_j \quad (\text{VI} - 40)$$

Here, $(\Delta_\lambda \log ZC)_P$ is the increment of the case that the whole one of the objective property P_j is unchangeable.

$$\begin{aligned} \log \lambda &= \Delta_\lambda \log Z(A+K) = (\Delta_\lambda \log Z(A+K)) \\ &+ \sum_b \frac{\partial \log Z(A+K)}{\partial \beta_b} \Delta_\lambda \beta_b \end{aligned} \quad (\text{VI} - 41)$$

Here, the suffix β expresses the condition that all β_b are constant. $\Delta_\lambda \beta_b$ is the increment of β_b under the condition that $A+K$ is decided.

Like the following relation as shown in the following equation, eq. (VI - 42), the conjugate force

$$\begin{aligned} kT \frac{\partial \log Z(A+K)}{\partial \beta_b} \text{ to } \beta_b \text{ is zero according to the condi-} \\ \text{tion described in the above described section (ii); there} \\ \text{is no conjugate force to } \beta_b \text{ that acts on } A+K \text{ from the} \\ \text{outside. Namely,} \\ \frac{\partial \log Z(A+K)}{\partial \beta_b} = 0 \end{aligned} \quad (\text{VI} - 42)$$

On the other hand, according to the condition described in the above described section (iii); after the value of β_b is decided, the state of energy of each assembly is decided independently, mechanically, mutually, and respectively. The following relation can be led as shown in the following equation, eq. (VI - 43).

$$Z(A+K) = ZA \cdot ZA \quad (\text{VI} - 43)$$

Therefore, the following relation is obtained as shown in the following equation, eq. (VI - 44).

$$(\Delta_\lambda \log Z(A+K))_\beta = \Delta_\lambda \log ZA_\beta + (\Delta_\lambda \log ZK)_\beta \quad (\text{VI} - 44)$$

Then, the following relation shown in the following equation, eq. (VI - 45), is obtained.

$$(\Delta_\lambda \log ZK)_\beta = 0 \quad (\text{VI} - 45)$$

Because, the procedure λ is performed only against A .

So, the following relation is obtained as shown in the following equation, eq. (VI - 46), according to the equations, eq. (VI - 41), eq. (VI - 42), eq. (VI - 44), and eq. (VI - 45).

$$\log \lambda = \Delta_\lambda \log Z(A+K) = \Delta_\lambda \log ZA_\beta \quad (\text{VI} - 46)$$

In the result, the two defined λ s in the above described section are equal to each other.

Development formula of λ concerning A and the quantity led from it: the λ of $A+K$ is developed especially to the objective assembly. At first, $-kT \log Z(A+K)$ is tried to develop to the form that is related to the assembly A only. From eq. (VI - 43) the following relation shown in the following equation, eq. (VI - 47), is obtained.

$$\log Z(A+K) = \log ZA + \log ZK \quad (\text{VI} - 47)$$

Next, $\log ZK$ can be rewritten as shown in the following equation, eq. (VI - 48), according to eq. (VI - 28).

$$\log ZK = \frac{1}{kT} \sum_b \int_{\beta_b(o)}^{\beta_b} \bar{\Pi}_{\beta_b}^K d\beta_b + \log ZK_{\beta(o)} \quad (\text{VI} - 48)$$

Here, $\bar{\Pi}_{\beta_b}^K$ expresses the mean force of the conjugate assembly K to β_b . And $K_{\beta(o)}$ expresses the assembly K decided by the condition that a set of β_b holds a constant value $\beta_b(o)$.

On the other hand, according to equations, eq. (VI - 27), eq. (VI - 42), and eq. (VI - 47), the following relation shown in the following equation, eq. (VI - 49), is valid.

$$\bar{\Pi}_{\beta_b}^A + \bar{\Pi}_{\beta_b}^K = 0 \quad (\text{VI} - 49)$$

Here, $\bar{\Pi}_{\beta_b}^A$ is mean force of the conjugate assembly A to β_b .

If eq. (VI - 49) is substituted in eq. (VI - 48), the following relation is obtained as shown in the following equation, eq. (VI - 50).

$$\log ZK = -\frac{1}{kT} \sum_b \int_{\beta_b(o)}^{\beta_b} \bar{\Pi}_{\beta_b}^A d\beta_b + \log ZK_{\beta(o)} \quad (\text{VI} - 50)$$

Moreover, when eq. (VI - 50) is substituted in eq. (VI

- 47), the following relation is given as shown in the following equation. eq. (VI - 51).

$$\log Z(A+K) = \log ZA - \frac{1}{kT} \sum_b \int_{\beta_b(o)}^{\beta_b} \bar{\pi}_{\beta_b}^A d\beta_b + \log ZK_{\beta(o)} \quad (\text{VI} - 51)$$

As $\log ZK_{\beta(o)}$ is constant, this equation is the one that $\log Z(A+K)$ is expressed by usage of the variable of A only.

Moreover, the following relation shown in the following equation, eq. (VI - 52) is obtained against $\log \lambda$ from eq. (VI - 29) and eq. (VI - 51).

$$\begin{aligned} \log \lambda &= \Delta_\lambda \log Z(A+K) \\ &= \Delta_\lambda \log ZA - \frac{1}{kT} \sum_b \Delta_\lambda \int_{\beta_b(o)}^{\beta_b} \bar{\pi}_{\beta_b(o)}^A \bar{\pi}_{\beta_b}^A d\beta_b \\ &= \Delta_\lambda \log ZA - \frac{1}{kT} \sum_b \int_{\beta_b(o)}^{\beta_b} \Delta_\lambda \bar{\pi}_{\beta_b}^A d\beta_b \\ &\quad - \frac{1}{kT} \sum_b \bar{\pi}_{\beta_b}^A \Delta_\lambda \beta_b \end{aligned} \quad (\text{VI} - 52)$$

Here, $\Delta_\lambda \beta_b$ and $\Delta_\lambda \bar{\pi}_{\beta_b}^A$ are the increments obtained by the procedure related to λ against parameter β_b and force $\bar{\pi}_{\beta_b}^A$.

Next, consider the thermal changes of $Z(A+K)$ and λ . At first, from eq. (VI - 42) and eq. (VI - 47), the following relation against the thermal change of $Z(A+K)$ is obtained as shown in the following equation, eq. (VI - 53).

$$\begin{aligned} \frac{\partial \log Z(A+K)}{\partial T} &= \left(\frac{\partial \log Z(A+K)}{\partial T} \right)_\beta \\ &+ \sum_b \frac{\partial \log Z(A+K)}{\partial \beta_b} \cdot \frac{\partial \beta_b}{\partial T} \\ &= \left(\frac{\partial \log ZA}{\partial T} \right)_\beta + \left(\frac{\partial \log ZK}{\partial T} \right)_\beta \end{aligned} \quad (\text{VI} - 53)$$

Or, if $\left(\frac{\partial \log ZK}{\partial T} \right)_\beta$ is expressed by usage of eq. (VI - 50), the following relation shown in the following equation, eq. (VI - 54), is obtained.

$$\begin{aligned} kT^2 \frac{\partial \log Z(A+K)}{\partial T} &= kT^2 \left(\frac{\partial \log ZA}{\partial T} \right)_\beta \\ &+ \sum_b \int_{\beta_b(o)}^{\beta_b} \bar{\pi}_{\beta_b(o)}^A \bar{\pi}_{\beta_b}^A d\beta_b \\ &- T \sum_b \int_{\beta_b(o)}^{\beta_b} \frac{\partial \bar{\pi}_{\beta_b}^A}{\partial T} d\beta_b + kT^2 \frac{\partial \log ZK_{\beta(o)}}{\partial T} \end{aligned} \quad (\text{VI} - 54)$$

Here, the differentiation coefficient under the condition that $A+K$ is decided is expressed without addition of suffix. But, the differentiation coefficient under the condition that all β_b is constant is expressed with addition of suffix.

Then, the thermal change of λ can be expressed as the following equation, eq. (VI - 55), according to equations, eq. (VI - 29) and eq. (VI - 54).

$$\begin{aligned} kT^2 \frac{\partial \log \lambda}{\partial T} &= kT^2 \Delta_\lambda \left(\frac{\partial \log ZA}{\partial T} \right)_\beta \\ &+ \sum_b \int_{\beta_b(o)}^{\beta_b} \Delta_\lambda \bar{\pi}_{\beta_b}^A d\beta_b + \sum_b \bar{\pi}_{\beta_b}^A \Delta_\lambda \beta_b \\ &- T \sum_b \int_{\beta_b(o)}^{\beta_b} \Delta_\lambda \frac{\partial \bar{\pi}_{\beta_b}^A}{\partial T} d\beta_b - T \sum_b \frac{\partial \bar{\pi}_{\beta_b}^A}{\partial T} \Delta_\lambda d\beta_b \end{aligned} \quad (\text{VI} - 55)$$

Of course, it is obtained directly when the partial differentiation of eq. (VI - 52) is carried out in regard to T .

On the other hand, the thermal change of λ that is defined in regard to the assembly A_β is given as shown in the following equation, eq. (VI - 56), according to equations, eq. (VI - 29), eq. (VI - 45), and eq. (VI - 47).

$$kT^2 \left(\frac{\partial \log \lambda}{\partial T} \right)_\beta = kT^2 \Delta_\lambda \left(\frac{\partial \log ZA}{\partial T} \right)_\beta \quad (\text{VI} - 56)$$

If eq. (VI - 56) is compared with eq. (VI - 55), the value of λ that is defined in regard to the two different

assemblies is equal as shown in the above described section. However, it is understood that the thermal change is different generally.

Discussion and Conclusion

The duplicated description of contents that are mentioned in the section of Experimental and Results is cut off except the important parts.

Several functions in thermodynamics: Helmholtz free energy F and internal energy U are fundamental quantity in thermodynamics. So, the relation between the two quantities and the Zustandsumme is considered. The physical meaning and the applying of Zustandsumme can be succeeded to connect with Helmholtz free energy or internal energy.

And the conjugate mean force to the parameter α_a is related to the free energy, and the parameter is found as an important point.

Also, it is led as other important point that the reversible work per mole of δ is equal to the chemical potential in thermodynamics.

According to Lewis, partial molar free energy, partial molar internal energy, and partial molar entropy are expressed as $\Delta_p \delta F$, $\Delta_p \delta U$, and $\Delta_p \delta S$ against \bar{F}^δ , \bar{U}^δ , and \bar{S}^δ respectively.

Next, $\mu^\delta = \frac{g}{\prod (\nu_g^\delta)^{\nu_g}}$ becomes another form as $\mu^\delta = \sum_g \nu_g \mu_g^\delta$

This physical meaning can be understood in comparison with the both relations. It is proved at the first step that this new theoretical treatment can expand into the fundamental theory of general chemical reaction. Namely, this theory is successful in an expansion as this example. Then, for example, the case that the extreme slight material $\delta_1, \dots, \delta_g, \dots$ are added into a large material system is considered. The chemical potential of the material that may be added later is not changed by the addition of any one in former time. Here, δ is composed with $\nu_1, \dots, \nu_g, \dots$ pieces of $\delta_1, \dots, \delta_g, \dots$ kinds of molecules, namely, it is expressed as $\delta = \sum_g \nu_g \delta_g$. In that case, the relation is set up similarly. Namely,

$\mu^\delta = \frac{g}{\prod (\nu_g^\delta)^{\nu_g}}$

The physical meaning is expressed by the above described relation. It can be understood that this relation is a truism in thermodynamics by an expansion of this theoretical treatment for chemical reaction.

Force, work, and energy: this theoretical treatment includes extreme large extent. However, only small part of this theoretical treatment is discussed in this section. Then, these quantities, force, work, and energy, are fundamental quantities in thermodynamics and mechanics. Then, these quantities must be tried to be defined by this new theoretical treatment. This theoretical treatment has one consideration that chemical reaction is occurred by collision of particle or molecule. Chemical species is one kind of particle at molecular level. So, the motion, movement, or behavior of particle is fundamental subject that is related to the probability of collision or passing through a surface in regard to time. Especially, in gaseous chemical reaction, temperature factor must be added. Generally, temperature factor or pressure factor is most important. But in this case that the reaction system exists at thermal equilibrium, this new theoretical treatment is operated at the first step. Moreover, the assembly exists at statistical equilibrium. Such simplification can be tried to apply and to expand this theoretical treatment as the result. If the system is not existed at thermal equilibrium, the theoretical treatment becomes extremely complicate and difficult. However, the consideration that the time existing at thermal equilibrium is extremely short may be applied to one solution of the problem. So, it is assumed as follows; the assembly is kept to exist at statistical equilibrium. And the internal parameter and the external parameter can be changeable independently, continuously, and mutually. The following relations can be expressed.

$-kT \frac{\partial \log ZC}{\partial \alpha_a} = -\bar{\Pi} \alpha_a$, and moreover,

$-kT \log \frac{ZC_{II}}{ZC_I} = \sum_a \int_{\alpha_a(I)}^{\alpha_a(II)} (-\bar{\Pi} \alpha_a d\alpha_a)$

are defined. Especially, the reversible work that the assembly shifts from state I to state II keeping to exist at statistical equilibrium is expressed by the right

side of the later formula. Then, the left side of the later formula is equal to the reversible work corresponding to the right side and becomes $-kT \log p^\delta$. The physical quantity, work, can be expressed by the two kinds of treatment. Similarly, $-kT \log q_\sigma^\delta$ can express the work required to shift δ from standard state to state σ . $-kT \log(\mathbb{H})_{\sigma(\delta)}$ or $-kT \log(\mathbb{H})_{\sigma(O)}$ is the reversible work that requires to make exist δ at σ certainly or not. Especially, according to the point that the three reversible works except $-kT \log p^\delta$ include the micro property, they can not correspond to any function that has been defined in thermodynamics. This point is important as the consideration that this theoretical treatment is new. Namely, the new treatment was tried to apply to chemical reaction.

Then, the four reversible works can be summarized as

$$-kT \log \lambda = \Delta_\lambda (-kT \log ZC)$$

or

$$-RT \log \lambda = \Delta_\lambda (-kT \log ZC)$$

Here, $\Delta_\lambda = \Delta_\lambda \cdot N_A$. This simplification is very convenient. The thermal change of ZC can be expressed as $kT^2 \frac{\partial \log ZC}{\partial T} = \bar{E}$. So, the thermal change of λ can be

expressed as $RT^2 \frac{\partial \log \lambda}{\partial T} = \Delta_\lambda \bar{E}$. These relations are

very interest in thermodynamics to develop this new theoretical treatment. The following conditions are very important. However, the above described explanation omitted to describe the detailed conditions for avoidance of the duplication.

Relative equation of p^δ at equilibrium: this expression and this definition of p^δ are basic and important in this new theoretical treatment. For example, the behavior of δ that is component of the assembly C^δ came into question. When δ can shift very rapidly to various states, $\delta^A, \delta^B, \dots$, the $ZC^{\delta^A}, ZC^{\delta^B}, \dots$ become the same value. As the Zustandsumme is the sum of Boltzmann's factor in regard to all possible states of the assembly, although the assembly exists at any state, it does not come into question.

$p^{\delta^A} = p^{\delta^B} = \dots$ Namely, when the state satisfies the relation described above, the state of $\delta, \delta^A, \delta^B, \dots$, exists at equilibrium with each other. $\delta^A, \delta^B, \dots$, is

composed with ν_a^A, ν_b^B, \dots , pieces of molecule, $\delta_a^A, \delta_b^B, \dots$. Namely, these relations, $\frac{a}{\Pi} (p^{\delta^A})^{\nu_a^A} = \frac{b}{\Pi} (p^{\delta^B})^{\nu_b^B} = \dots$, are obtained from those relations, $\delta^A = \sum_a \nu_a^A \delta_a^A$, $\delta^B = \sum_b \nu_b^B \delta_b^B, \dots$ and $p^\delta = \frac{g}{\Pi} (p^{\delta^g})^{\nu_g}$.

These expressions are placed on the consideration of this theoretical treatment. The chemical species is composed with molecule. This consideration is placed on molecular level and is not placed on the atomic level. At the next step, the author wants to consider atomic level including elementary particle. Of course, electrostatic force, magnetic force, orbital of electron, many physical properties or quantities, these physical moments and interactions, and others can develop this theoretical treatment to chemical reaction.

λ for the assembly held the variable external parameter: to be satisfied in the case that the external parameter is changeable to the assembly requires to make the theory and the definition the expansile and general form. As such an expansion or generalization produces rarely the extreme complication, the procedure is not so easy. Fortunately this case is successful. The λ described in the above section is related to the assembly in the limitation that the external parameter is kept at constant. Then, the case that the limitation is loosened slightly is considered in this section. Namely, when the external parameter of the objective assembly is not always kept at constant, try to expand to definition and the theory of λ .

Then,

(i) the external parameter had extensive property changes about each one of A and K , but the sum of β_b of A and that of K is unchangeable. And the external parameter except this kind is unchangeable about each one of A and K .

(ii) the conjugate force to β_b that acts on $A+K$ from the outside does not exist.

(iii) the energy state of each assembly is decided by decision of value of β_b mechanically and independently.

The movement of piston in cylinder that is an ideal model is taken for one explanation. Thus, this theory can apply to one understandable model. This model of piston and cylinder is nice and useful one for explana-

tion of behavior of gas. Sometimes $PV = nRT$, work and force, friction and heat, adiabatic expansion, partial differentiation by physical quantity, and so on. The example that the three conditions are satisfied is the assembly $A+K$ separated by piston in cylinder. The gaseous part A and K are separated by piston in cylinder. So the assembly is composed with A and K . Then, the next conditions are very important. The energy state of each gaseous part is decided by the external parameter of A . Moreover, the conjugate force to the external parameter does not act on it from the outside. The $A+K$ is special assembly of the assemblies treated in the above described sections. The definition and the theory are valid to the $A+K$. Thus, this theory was possible to expand. Also, when β_b does not change, this is valid to the assembly A alone. Such an assembly is expressed as A_β . As the assembly that $\log \lambda = \Delta_\lambda \log ZC$ is valid, the selection of either $A+K$ or A_β decides the important point that λ is defined against either the assembly $A+K$ or A_β . Later, the various formulas obtained in this discussed process may be tried to be expressed using the various functions in thermodynamics in comparison with λ of A_β . This trial that is interesting in consideration among quantum statistical mechanics, thermodynamics, quantum mechanics and statistical mechanics is one basic and thoughtful procedure for expanding this theoretical treatment to generalization.

Equivalence between λ of the assembly $A+K$ and λ of the assembly A_β : it is discussed in this section that the value of λ defined by two kinds of definition is equal with each other. As the result of discussion, the both values obtained in regard to the assembly $A+K$ and the assembly A_β are equal mutually from the development of the relative equations according to these definitions.

The $\log \lambda$ of the assembly $A+K$ can be expressed as the relationship shown in the following equation according to the relationship described in the previous paper²⁴.

$$\log \lambda = (\Delta_\lambda \log Z(A+K)) + \sum_b \frac{\partial \log Z(A+K)}{\partial \beta_b} \Delta \lambda \beta_b$$

Here, $\Delta \lambda \beta_b$ is the increment of β_b under the condition that $A+K$ is decided. And, suffix β means the condition that all β_b are constant. Thus, the relation among λ , $A+K$, β_b , and $\Delta \lambda \beta_b$ is obtained. Moreover, the conjugate

force to β_b is zero. So, $Z(A+K) = ZA \cdot ZK$. Then, $(\Delta_\lambda \log Z(A+K))_\beta$ is equal to $\Delta_\lambda \log ZA_\beta + (\Delta_\lambda \log ZK)_\beta$. And $(\Delta_\lambda \log ZK)_\beta$ is equal to zero, because, the procedure λ is operated only against A . Then, $\log \lambda$ is equal to $\Delta_\lambda \log Z(A+K)$ or $\Delta_\lambda \log ZA_\beta$ respectively. Namely, it is recognized that the value between the two λ s is equal.

Development formula of λ concerning A and the quantity led from it: the λ of the assembly $A+K$ is tried to develop in regard to the objective assembly A . λ can be defined by Zustandsumme. Its procedure is the same to the case of complete equilibrium. Also, the theory related to λ can be applied to the assembly existed at thermal equilibrium. However, such an assembly is not always free from any limitation. Here is one micro limitation in assumption of having a constant composition. The complete free ensemble or assembly is the establishment of formation. It is natural that formation is different from unformation exactly. So, the difference on the making difference is nothing but the limitation. Then, such a consideration is developed as follows: to avoid the complication, $-kT \log Z(A+K)$ is developed in regard to the assembly A alone.

$$\log Z(A+K) = \log Z + \log ZK$$

$$\log ZK = \frac{1}{kT} \sum_b \int_{\beta_b(o)}^{\beta_b} \bar{\pi}_{\beta_b}^K d\beta_b + \log ZK_{\beta(o)}$$

Here, $\bar{\pi}_{\beta_b}^K$ is mean force of the assembly K conjugated to β_b . $K_{\beta(o)}$ is the assembly K that a set of β_b has one value of $\beta_b(o)$. Also, $\bar{\pi}_{\beta_b}^A + \bar{\pi}_{\beta_b}^K = 0$. Here, $\bar{\pi}_{\beta_b}^A$ is mean force of the assembly A conjugated to β_b . Therefore, from the relations described above and in the previous paper,

$$\log Z(A+K) = \log ZA - \frac{1}{kT} \sum_b \int_{\beta_b(o)}^{\beta_b} \bar{\pi}_{\beta_b}^A d\beta_b + \log ZK_{\beta(o)}$$

$\log Z(A+K)$ can be expressed by only variable of A , as $\log ZK_{\beta(o)}$ is constant. Moreover,

$$\log \lambda = \Delta_\lambda \log ZA - \frac{1}{kT} \sum_b \int_{\beta_b(o)}^{\beta_b} \Delta_\lambda \bar{\pi}_{\beta_b}^A d\beta_b - \frac{1}{kT} \sum_b \bar{\pi}_{\beta_b}^A \Delta \lambda \beta_b \quad (a)$$

Here, $\Delta\lambda$, β_b and $\Delta\lambda$, $\bar{\Pi}_{\beta_b}^A$ are the increments of parameter β_b and force $\bar{\Pi}_{\beta_b}^A$ by the procedure related to λ . Next, consider the thermal change of $Z(A+K)$ and λ in order. What thermal change does occur in the assembly?

$$\frac{\partial \log Z(A+K)}{\partial T} = \left(\frac{\partial \log ZA}{\partial T}\right)_{\beta} + \left(\frac{\partial \log ZK}{\partial T}\right)_{\beta} \quad (b)$$

or

$$kT^2 \frac{\partial \log Z(A+K)}{\partial T} = kT^2 \left(\frac{\partial \log ZA}{\partial T}\right)_{\beta} + \sum_b \int_{\beta_b(o)}^{\beta_b} \bar{\Pi}_{\beta_b}^A d\beta_b - T \sum_b \int_{\beta_b(o)}^{\beta_b} \frac{\partial \bar{\Pi}_{\beta_b}^A}{\partial T} d\beta_b + kT^2 \frac{\partial \log ZK_{\beta(o)}}{\partial T} \quad (c)$$

The differentiation coefficient in the condition that $A+K$ is decided does not add suffix. And it in the condition that all β_b is constant adds suffix. The former equation, (b), can be expressed as the sum of thermal change of each assembly using partial differentiation in a simple form. Such a development of theoretical treatment is successful to application and generalization. Next, what thermal change does occur in λ ?

$$kT^2 \frac{\partial \log \lambda}{\partial T} = kT^2 \Delta\lambda \left(\frac{\partial \log ZA}{\partial T}\right)_{\beta} + \sum_b \int_{\beta_b(o)}^{\beta_b} \Delta\lambda \bar{\Pi}_{\beta_b}^A d\beta_b + \sum_b \bar{\Pi}_{\beta_b}^A \Delta\lambda \beta_b - T \sum_b \int_{\beta_b(o)}^{\beta_b} \Delta\lambda \frac{\partial \bar{\Pi}_{\beta_b}^A}{\partial T} d\beta_b - T \sum_b \frac{\partial \bar{\Pi}_{\beta_b}^A}{\partial T} \Delta\lambda \beta_b \quad (d)$$

This partial differentiation of temperature against T becomes the form of sum according to eq. (c). This relation is obtained directly by partial differentiation related to T against eq. (a) described above. On the other hand, in the case that λ is defined in regard to the assembly A_{β} , the thermal change of the defined λ is given as follows;

$$kT^2 \left(\frac{\partial \log \lambda}{\partial T}\right)_{\beta} = kT^2 \Delta\lambda \left(\frac{\partial \log ZA}{\partial T}\right)_{\beta} \quad (e)$$

Here, in comparison between (d) and (e), the value of λ defined in the two different assemblies is equal with each other, but generally the thermal change of λ is not equal with each other. This subject is important to

understand the effect of temperature factor against the assembly. In such an analysis of physical meaning, this theoretical treatment can achieve one purpose. It is successful to analyze one part of property of assembly or ensemble. Of course, the assembly or the ensemble has other properties that may be tried to analyze. Indeed, the generalization is very difficult.

Summary

Some fundamental considerations of this new theoretical treatment are tried to expand into the connection with quantum statistical mechanics and thermodynamics. Of course, the definition and the theory related to them are decided and considered.

Several functions in thermodynamics: the relation among Helmholtz's free energy, internal energy, and Zustandsumme is considered and defined connecting with statistical mechanics and thermodynamics. Also, chemical potential, reversible work, partial molar free energy, partial molar internal energy, and partial molar entropy can be led by this new theoretical treatment.

Force, work, and energy: the work that the assembly shifts from state I to state II holding to exist at statistical equilibrium is expressed as reversible work. And the relation between λ and ZC is studied in general case that the external parameter of the assembly is constant. The relation between four functions, ρ^{δ} , $\mathbf{q}_{\sigma}^{\delta}$, $\Theta_{\sigma}(\delta)$, and $\Theta_{\sigma(o)}$, defined by ratio of Zustandsumme and reversible work is considered.

Relative equation of ρ^{δ} at equilibrium: if δ^A , δ^B , ... is composed with ν_a^A , ν_b^B , ... pieces of molecule, $\bar{\Pi}(\rho^{\delta a}) \nu_a^A = \bar{\Pi}(\rho^{\delta b}) \nu_b^B = \dots$ are set up.

λ for the assembly held the variable external parameter: the definition and the theory of λ expand into the assembly that the external parameter is not always constant. The procedure λ is added to the assembly A related to other assembly K . (i) External parameter had extensive property changes in regard to each one of A and K , but the sum of β_b of A and that of K is unchangeable. (ii) The conjugate force to β_b that acts on $A+K$ from the outside does not exist. (iii) As the value of β_b is decided, energy state of each assembly is decided independently, respectively, and mechanically

with each other. All the definition and the theory are set up for $A+K$. Also, if β_b is unchangeable, it is set up for the assembly alone.

Equivalence between λ of the assembly $A+K$ and λ of the assembly A_β : it is considered that λ of the assembly $A+K$ is equivalent to λ of the assembly A_β .

$$\log \lambda = \Delta_\lambda \log Z(A+K) = (\Delta_\lambda \log Z(A+K))$$

$$+ \sum_b \frac{\partial \log Z(A+K)}{\partial \beta_b} \Delta_\lambda \beta_b$$

$$\text{Here, } kT \frac{\partial \log Z(A+K)}{\partial \beta_b} = 0 \quad \text{Then, } \frac{\partial \log Z(A+K)}{\partial \beta_b} = 0$$

$$\text{Also, } Z(A+K) = ZA \cdot ZK \quad \text{Therefore, } (\Delta_\lambda \log Z(A+K))_\beta = \Delta_\lambda \log ZA_\beta + (\Delta_\lambda \log ZK)_\beta \quad \text{Here, } (\Delta_\lambda \log ZK)_\beta = 0$$

$$\text{Also, } \log \lambda = \Delta_\lambda \log Z(A+K) = \Delta_\lambda \log ZA_\beta$$

So, the values of two λ s defined as the above description are equal mutually.

Development formula of λ concerning A and the quantity led from it:

$$\log ZK = \frac{1}{kT} \sum_b \int_{\beta_b(o)}^{\beta_b} \bar{\Pi}_{\beta_b}^K d\beta_b + \log ZK_{\beta(o)}$$

$$\log \lambda = \Delta_\lambda \log ZA - \frac{1}{kT} \sum_b \int_{\beta_b(o)}^{\beta_b} d\beta_b' - \frac{1}{kT} \sum_b \bar{\Pi}_{\beta_b}^A \Delta_\lambda \beta_b$$

Next, thermal change of $Z(A+K)$ and λ is considered.

$$kT^2 \frac{\partial \log Z(A+K)}{\partial T} = kT^2 \left(\frac{\partial \log ZA}{\partial T} \right)_\beta + \sum_b \int_{\beta_b(o)}^{\beta_b} \bar{\Pi}_{\beta_b}^A d\beta_b - T \sum_b \int_{\beta_b(o)}^{\beta_b} \frac{\partial \bar{\Pi}_{\beta_b}^A}{\partial T} d\beta_b + kT^2 \frac{\partial \log ZK_{\beta(o)}}{\partial T}$$

And, thermal change of λ is studied.

$$kT^2 \frac{\partial \log \lambda}{\partial T} = kT^2 \Delta_\lambda \left(\frac{\partial \log ZA}{\partial T} \right)_\beta + \sum_b \int_{\beta_b(o)}^{\beta_b} \Delta_\lambda \bar{\Pi}_{\beta_b}^A d\beta_b + \sum_b \bar{\Pi}_{\beta_b}^A \Delta_\lambda \beta_b$$

$$-T \sum_b \int_{\beta_b(o)}^{\beta_b} \Delta_\lambda \frac{\partial \bar{\Pi}_{\beta_b}^A}{\partial T} d\beta_b - T \sum_b \frac{\partial \bar{\Pi}_{\beta_b}^A}{\partial T} \Delta_\lambda d\beta_b$$

Thermal change of λ defined in regard to the assembly A_β is studied.

$$kT^2 \left(\frac{\partial \log \lambda}{\partial T} \right)_\beta = kT^2 \Delta_\lambda \left(\frac{\partial \log ZA}{\partial T} \right)_\beta$$

As the result, the value of λ defined in regard to two different assemblies is equal, but thermal change is generally different.

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化学反応の理論的取扱
 第6報 量子統計力学と熱力学との関係
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 (昭和59年10月3日受理)

新理論的取扱のいくつかの基礎的考察は量子統計力学と熱力学の関連への展開を試み、勿論、定義と理論をきめ考察した。

熱力学のいくつかの関数：ヘルムホルツ自由エネルギー、内部エネルギー、状態間との関係を考察し、統計力学と熱力学との関連において定義し、化学ポテンシャル、可逆の仕事、偏分分子自由エネルギー、偏分分子内部エネルギー、偏分分子エントロピーが新理論的取扱で導きえた。

力、仕事、エネルギー：集団が状態 I から II へ統計的平衡を保ちつつ移る仕事は可逆の仕事で表わされる。λ と ZC の関係を集団の外部パラメーターが一定である一般の場合につき研究し、状態と可逆の仕事の比で定義された ρ^δ , q_σ^δ , $\Theta_\sigma(\delta)$, $\Theta_\sigma(0)$ を考察した。

$$\text{平衡時の } \rho^\delta \text{ の関係式: } \frac{a}{\prod (\rho_a^\delta)^{\nu_a^A}} = \frac{b}{\prod (\rho_b^\delta)^{\nu_b^B}} = \dots$$

可変外部パラメーターをもつ集団の λ : λ の定義と理論を外部パラメーターが必ずしも一定でない集団へ展開し、操作 λ は他の集団 K と関係ある集団 A へ加えられ、(1) 広がり性質をもつ外部パラメーターは A と K 個個に変わるが A の β_b と K のそれとの和は不変、(2) 外部から A+K に作用する β_b の共役力は不存、(3) β_b がきまり各集団のエネルギー状態はそれぞれ力学的に相互に無関係にきまる。

集団 A+K と A_β の λ の等価: $\log \lambda = \Delta_\lambda \log Z(A+K)$,

$$kT \frac{\partial \log Z(A+K)}{\partial \beta_b} = 0, \quad \frac{\partial \log Z(A+K)}{\partial \beta_b} = 0, \quad Z(A+K) = ZA \cdot ZK, \quad \text{故に} \quad (\Delta_\lambda \log Z(A+K))_\beta =$$

$$\Delta_\lambda \log ZA_\beta + (\Delta_\lambda \log ZK)_\beta, \quad (\Delta_\lambda \log ZK)_\beta = 0, \quad \log \lambda = \Delta_\lambda \log Z(A+K) = \Delta_\lambda \log ZA_\beta. \quad 2\lambda \text{ は等価}$$

A に関する λ の展開式とそれから導かれた量:

$$\log ZK = \frac{1}{kT} \sum_b \int_{\beta_b(0)}^{\beta_b} \bar{\pi}_{\beta_b}^K d\beta_b + \log ZK_{\beta_b(0)} \quad \log \lambda = \Delta_\lambda \log ZA - \frac{1}{kT} \sum_b \int_{\beta_b(0)}^{\beta_b} \Delta_\lambda \bar{\pi}_{\beta_b}^A d\beta_b$$

$$- \frac{1}{kT} \sum_b \bar{\pi}_{\beta_b}^A \Delta_\lambda \beta_b$$

次に、 $Z(A+K)$ と λ の温度変化,

$$kT^2 \frac{\partial \log Z(A+K)}{\partial T} = kT^2 \left(\frac{\partial \log ZA}{\partial T} \right)_\beta + \sum_b \int_{\beta_{b(0)}}^{\beta_b} \bar{\pi}_{\beta_b}^A d\beta_b - T \sum_b \int_{\beta_{b(0)}}^{\beta_b} \frac{\partial \bar{\pi}_{\beta_b}^A}{\partial T} d\beta_b + kT^2 \frac{\partial \log ZK^{\beta(0)}}{\partial T}$$

λ の温度変化,

$$kT^2 \frac{\partial \log \lambda}{\partial T} = kT^2 \Delta_\lambda \left(\frac{\partial \log ZA}{\partial T} \right)_\beta + \sum_b \int_{\beta_{b(0)}}^{\beta_b} \Delta_\lambda \bar{\pi}_{\beta_b}^A d\beta_b + \sum_b \bar{\pi}_{\beta_b}^A \Delta_\lambda \beta_b - T \sum_b \int_{\beta_{b(0)}}^{\beta_b} \Delta_\lambda \frac{\partial \bar{\pi}_{\beta_b}^A}{\partial T} d\beta_b - T \sum_b \frac{\partial \bar{\pi}_{\beta_b}^A}{\partial T} \Delta_\lambda \beta_b$$

集団 A_β に関し定義された λ の温度変化,

$$kT^2 \left(\frac{\partial \log \lambda}{\partial T} \right)_\beta = kT^2 \Delta_\lambda \left(\frac{\partial \log ZA}{\partial T} \right)_\beta$$

結果として、2 異集団に関し定義された λ の値は等しいが、温度変化は一般に異なる。