

One Theoretical Treatment of Chemical Reaction

Part 7 Relation to Quantum Statistical Mechanics and Thermodynamics Partially

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(Received September 30, 1985)

Introduction

One part of basic consideration of the new theoretical treatment to chemical reaction is reported relating to connection with quantum statistical mechanics and thermodynamics. Now, many problems are considered in regard to this objective. So, the problems treated from among these many problems on this paper are as follows; (1) thermodynamical type of λ against the assembly which possesses the variable external parameter, and thermodynamical type of the quantity related to it, (2) one part of thermodynamical type of λ against the assembly and one part of the quantity led from it.

Some theoretical treatments^{1~23)} were published on these viewpoints.

Experimental and Results, Gedanken Experiment

Thermodynamical types of both λ against the assembly which possesses the variable external parameter and the quantity related to it: according to $F = -kT \log ZC^{23})$ and $U = kT^2 \frac{\partial \log ZC^{23})}{\partial T}$, Helmholtz's free energy and internal energy of the assembly $A + K$, A , or $K_{\beta(O)}$ can be expressed as follows;

$$F = -kT \log Z (A + K) \quad (\text{VII} - 1)$$

$$F_A = -kT \log Z A \quad (\text{VII} - 2)$$

$$F_{K\beta(O)} = -kT \log Z K_{\beta(O)} \quad (\text{VII} - 3)$$

$$U = kT^2 \frac{\partial \log Z (A + K)}{\partial T} \quad (\text{VII} - 4)$$

$$U_A = kT^2 \left(\frac{\partial \log Z A}{\partial T} \right)_{\beta} \quad (\text{VII} - 5)$$

$$U_{K\beta(O)} = kT^2 \frac{\partial \log Z K_{\beta(O)}}{\partial T} \quad (\text{VII} - 6)$$

$$\text{And if } \log Z (A + K)^{23}), \log \lambda^{23}), kT^2 \frac{\partial \log Z (A + K)^{23})}{\partial T},$$

$$\text{and } kT^2 \frac{\partial \log \lambda}{\partial T} \text{ are rewritten simply by usage of } F,$$

U , and π_{β} , they can be expressed as follows;

$$F = F_A + \sum_b \int^{\beta_b} \Pi_{\beta b}^A d\beta_b + F_{K\beta(O)} \quad (\text{VII} - 7)$$

$$\begin{aligned} -kT \log \lambda = \Delta_{\lambda} F_A + \sum_b \int^{\beta_b} \Delta_{\lambda} \Pi_{\beta b}^A d\beta_b \\ + \sum_b \Pi_{\beta b}^A \Delta_{\lambda} \beta_b \end{aligned} \quad (\text{VII} - 8)$$

$$\begin{aligned} U = F - T \frac{\partial F}{\partial T} = U_A + \sum_b \int^{\beta_b} d\beta_b \\ - T \sum_b \int^{\beta_b} \frac{\partial \Pi_{\beta b}^A}{\partial T} d\beta_b + U_{K\beta(O)} \end{aligned} \quad (\text{VII} - 9)$$

$$\begin{aligned}
 kT^2 \frac{\partial \log \lambda}{\partial T} &= \Delta_\lambda U_A + \sum_b \int_{\beta_b(O)}^{\beta_b} \Delta_\lambda \Pi_{\beta b}^A d\beta_b \\
 &+ \sum_b \Pi_{\beta b}^A \Delta_\lambda \beta_b - T \sum_b \int_{\beta_b(O)}^{\beta_b} \Delta_\lambda \frac{\partial \Pi_{\beta b}^A}{\partial T} d\beta_b \\
 &- T \sum_b \frac{\partial \Pi_{\beta b}^A}{\partial T} \Delta_\lambda \beta_b \quad (VII-10)
 \end{aligned}$$

Thermodynamical types of both λ against the assembly Ap and the quantity led from it: when the thermodynamical types of

$$-kT \log Z(A+K), -kT \log \lambda, kT^2 \frac{\partial \log Z(A+K)}{\partial T}$$

and $kT^2 \frac{\partial \log \lambda}{\partial T}$ which are developed as regards the

assembly A are corresponded to general used thermodynamic function in the above description, $\lambda \equiv p^\delta$ and $A \equiv Ap$ are valid. Namely, the volume V_A is only one parameter of A . And the pressure P_A which is conjugated to it is not depended upon V_A and T . Also, P_A is kept at constant. In this case, $\beta \equiv V_A$, $\Pi^A \equiv P_A = \text{constant}$, and $\lambda \equiv p^\delta$ are valid. Namely,

$$-RT \log \lambda = \mu^\delta \text{ is valid, and } -\Pi_{\alpha A} = \frac{\partial F^{23}}{\partial \alpha_A}, \text{ eq.}$$

(VII-7), eq. (VII-8), eq. (VII-9), and eq. (VII-10) are expressed respectively as follows;

$$P_A = - \left(\frac{\partial F_A}{\partial V_A} \right) \quad (VII-11)$$

$$F = F_A + P_A V_A + F_{K,V_A} = 0 \quad (VII-12)$$

$$\mu^\delta = \bar{F}_A^\delta + P_A \bar{V}_A^\delta \quad (VII-13)$$

$$U = F - T \frac{\partial F}{\partial T} = U_A + P_A V_A + U_{K,V_A} = 0 \quad (VII-14)$$

$$\mu^\delta - T \frac{\partial \mu^\delta}{\partial T} = \bar{V}_A^\delta + P_A \bar{V}_A^\delta \quad (VII-15)$$

Here, $\frac{1}{V_A} = 0$ or $U_{K,V_A} = 0$ expresses the value of $F_{K,\beta(O)}$ or $U_{K,\beta(O)}$ respectively in $\beta(O) = \bar{V}_A(O) = 0$.

$$\bar{F}_A^\delta = \Delta p^\delta F_A \quad (VII-16)$$

$$\bar{U}_A^\delta = \Delta p^\delta U_A \quad (VII-16)$$

$$\bar{V}_A^\delta = \Delta p^\delta \bar{V}_A \quad (VII-18)$$

The eq. (VII-16), eq. (VII-17), or eq. (VII-18) is partial molar quantity at constant pressure that the condition is Ap .

The variable part, $F_A + P_A V_A$, of F in eq. (VII-12) is called as free energy of Gibbs, G_A . Also, the variable part, $U_A + P_A V_A$, of U in eq. (VII-14) is called as enthalpy X_A . Consequently, $\bar{F}_A^\delta + P \bar{V}_A^\delta$ in eq. (VII-14) is similar to partial molar quantity \bar{G}_A of G_A . $U_A + P \bar{V}_A^\delta$ in eq. (VII-15) is similar to partial molar quantity \bar{X}_A^δ of X_A .

Namely,

$$G_A = F_A + P_A V_A \quad (VII-19)$$

$$X_A = U_A + P_A V_A \quad (VII-20)$$

$$\bar{G}_A^\delta = \bar{F}_A^\delta + P_A \bar{V}_A^\delta \quad (VII-21)$$

$$\bar{X}_A^\delta = \bar{U}_A^\delta + P_A \bar{V}_A^\delta \quad (VII-22)$$

If these usual thermodynamic functions are used, these above described equations, eq. (VII-11), eq. (VII-13), eq. (VII-14), and eq. (VII-15), are rewritten respectively as follows;

$$\left(\frac{\partial G_A}{\partial P_A} \right)_T = \bar{V}_A \quad (VII-23)$$

$$\mu^\delta = \bar{G}_A^\delta \quad (VII-24)$$

$$G_A - T \frac{\partial G_A}{\partial T} = X_A \quad (VII-25)$$

$$\mu^\delta - T \frac{\partial \mu^\delta}{\partial T} = \bar{X}_A^\delta \quad (VII-26)$$

Moreover, the following equation, eq. (VII-27), is obtained from both eq. (VII-23) and eq. (VII-24) as follows;

$$\left(\frac{\partial \mu^\delta}{\partial P_A} \right)_T = \bar{V}_A^\delta \quad (VII-27)$$

Also, the entropy S_A against part of the assembly A is expressed according to $S = - \frac{\partial F^{23}}{\partial T}$ as follows;

$$S_A = - \left(\frac{\partial F_A}{\partial T} \right)_{V_A} \quad (VII-28)$$

Discussion and Conclusion

As the section of experimental and results is most important in this paper, the major part of the limited pagination for one report is used predominantly for that section.

that section.

In regard to eq. (VII - 5), $U_A = kT^2 \left(\frac{\partial \log Z_A}{\partial T} \right)_{\beta}$:

the external parameter must be kept at constant when the partial differentiation is made to calculate the internal energy of the assembly as regards eq. (VII - 5). This condition is one condition which is assumed in general equation, $U = kT^2 \frac{\partial \log ZC}{\partial T}$.

In regard to eq. (VII - 23), $\left(\frac{\partial G_A}{\partial P_A} \right)_T = \overline{V}_A$:

the following equation eq. (VII - A),

$$\left(\frac{\partial G}{\partial P_A} \right)_T = \left(\frac{\partial F}{\partial V_A} \right)_T \left(\frac{\partial V_A}{\partial P_A} \right)_T + P_A \left(\frac{\partial V_A}{\partial P_A} \right)_T + V_A \quad (\text{VII - A})$$

is obtained from eq. (VII - 19), $G_A = F_A + P_A \overline{V}_A$.

And, if eq. (VII - 11), $P_A = - \left(\frac{\partial F_A}{\partial \overline{V}_A} \right)_T$, is sub-

stituted in eq. (VII - A), eq. (VII - 23), $\left(\frac{\partial G_A}{\partial P_A} \right)_T = \overline{V}_A$, is obtained.

In regard to eq. (VII - 25), $G_A - T \frac{\partial G_A}{\partial T} = X_A$:

if $F = F_A + P_A \overline{V}_A + F_{K, V_A} = 0$ is substituted in eq.

(VII - 12), eq. (VII - 14), $U = F - T \frac{\partial F}{\partial T} = U_A +$

$P_A \overline{V}_A + U_{K, V_A} = 0$, the following equation, eq. (VII

(VII - B),

$$G_A + F_{K, V_A} = 0 - T \frac{\partial F_{K, V_A} = 0}{\partial T} = X_A + U_{K, V_A} = 0 \quad (\text{VII - B})$$

is obtained from both eq. (VII - 19),

$G_A = F_A + P_A \overline{V}_A$, and eq. (VII - 20),

$$X_A = U_A + P_A \overline{V}_A.$$

And, as one special case of $U = F - T \frac{\partial F}{\partial T}$, the fol-

lowing equation, eq. (VII - C),

$$F_{K, V_A} = 0 - T \frac{\partial F_{K, V_A} = 0}{\partial T} = U_{K, V_A} \quad (\text{VII - C})$$

is valid. Also, eq. (VII - 25), $G_A - T \frac{\partial G_A}{\partial T} = X_A$

is obtained from both eq. (VII - B) and eq. (VII - C).

The several selected subjective points that must be understood at the first step are considered as mentioned above.

Summary

Thermodynamical type of λ against the assembly which possesses the variable external parameter is shown. Also, thermodynamical type of the quantity which is related to it is shown. Moreover, one part of thermodynamical type of λ against the assembly A_p is shown. Also, one part of thermodynamical type of the quantity which is led from it is shown.

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Foot note — As a pagination for one report was limited by budget, sections of summary, introduction, discussion and conclusion, and experimental and results should be shortened in that order.

化学反応の理論的取扱

第7報 量子統計力学と熱力学一部との関係

堀 津 圭 佑

(昭和60年9月30日受理)

新理論的取扱のうち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、前報に引続き発展させた。

種々の外部パラメーターをもつ集団に対する λ の熱力学的型を示した。また、それと関係ある量の熱力学的型も示した。さらに、集団 A_p に対する λ の熱力学的型の一部も示した。また、それから導かれた量の熱力学的型の一部も示した。