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One Theoretical Treatment of Chemical Reaction

Part 8 Relation to Quantum Statistical Mechanics and Thermodynamics Partially

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Introduction

There are various studies on chemical reaction from each special viewpoint. However, this new theroretical treatment is different from these published treatments by other investigators. Then, one part of basic consideration of the new theroetical treatment to chemical reaction is published relating to connection with quantum statistical mechanics and thermodynamics. Of course, there are many problems which are related to this objective. The one part from among many problems was published on the previous papers.[18~24] New, both one part of thermodynamical type of λ against the assembly Ap and one part of thermodynamical type of the quantity led from it were reported on the previous paper.[23] Then the other rest parts which are related to two thermodynamical types are reported on this paper.

Some investigators[1~23] published each theory on various viewpoints.

Experimental and Results, Gedanken Experiment

This section is referred to the corresponding section on the previous paper.[24] Namely, this part is the rest part unpublished of the section shown as the following description.

Thermodynamical type of λ against the assembly Ap and thermodynamical type of the quantity led from it: the relations expressed as the following several equations, from eq. (VIII – 1) to eq. (VIII – 5), are shown on the previous paper. Free energy of Helmholtz, F, and internal energy, U, are given by the fol-following equations, eq. (VIII – 1) and eq. (VIII – 2). This deviation is abbreviated here, because it was shown on the previous paper.[23]

$$F = - kT \log ZC \qquad \text{(VIII – 1)}$$

$$U = kT^2 \frac{\partial \log ZC}{\partial T} \qquad \text{(VIII – 2)}$$

Also, the following equation, eq. (VIII – 3), is derived from the equations, eq. (VIII – 1) and eq. (VIII – 2).

$$U = F - T \frac{\partial E}{\partial T} \qquad \text{(VIII – 3)}$$

And, the following equation, eq. (VIII – 4), is shown on the previous paper.[23] S or T is entropy or thermodynamic temperature respectively. This deviation is abbreviated here, as it was shown on the previous paper.[23]

$$F = U - TS \qquad \text{(VIII – 4)}$$

Moreover, the following equation, eq. (VIII – 5), is derived from the equations, eq. (VIII – 3) and eq. (VIII – 4).

$$S = - \frac{\partial F}{\partial T} \qquad \text{(VIII – 5)}$$

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So, the entropy S_A against part of the assembly A is expressed as the following equation, eq. (VIII – 6), according to the equation, eq. (VIII – 5).

$$S_A = -\left(\frac{\partial F_A}{\partial T}\right)_{V_A} \qquad \text{(VIII – 6)}$$

At first, the following equation, eq. (VIII – 7), is derived from the following equation, eq. (VIII – 8).

$$S_A = -\frac{\partial G_A}{\partial T} \qquad \text{(VIII – 7)}$$

$$P_A = -\left(\frac{\partial F_A}{\partial \mathbb{V}_A}\right)_T \qquad \text{(VIII – 8)}$$

The equation, eq. (VIII – 8), was shown on the previous paper.[24] As the derivation uses the space, it is abbreviated here. And, the following equation, eq. (VIII – 10), is derived from the following equations, eq. (VIII – 7) and eq. (VIII – 10). The equation, eq. (VIII – 9), was shown on the previous paper in analogy with eq. (VIII – 8).

$$G_A - T\frac{\partial G_A}{\partial T} = X_A \qquad \text{(VIII – 9)}$$

$$G_A + TS_A = X_A \qquad \text{(VIII – 10)}$$

Also, the following equation, eq. (VIII – 11), is derived from the equations, eq. (VIII – 7) and eq. (VIII – 12) shown on the previous paper.[24]

$$\overline{S}_A^{\delta} = -\frac{\partial \mu^{\delta}}{\partial T} \qquad \text{(VIII – 11)}$$

Moreover, the following equation, eq. (VIII – 13) is derived from the equations, eq. (VIII – 10) and eq. (VIII – 12).

$$\mu^{\delta} = \overline{G}_A^{\delta} \qquad \text{(VIII – 12)}$$

$$\mu^{\delta} + T\overline{S}^{\delta} = \overline{X}_A^{\delta} \qquad \text{(VIII – 13)}$$

Here, both partial differential coefficient and partial molar quantity that suffix are not subscribed are all related to the decided condition of AP, namely the coefficient and the quantity are related to constant pressure.

Then, to be convenient for applications at late time, suffix A of the above described relation equations related to partial molar quantity of A are rewritten to suffix P for express distinctly the condition of constant pressure. Namely, the subscript used P instead of suffix A. These equations, eq. (VIII – 12), eq. (VIII – 11), and eq. (VIII – 13), are rewritten to the following equations, eq. (VIII – 14), eq. (VIII – 15), and eq. (VIII – 16), respectively.

$$\mu^{\delta} = \overline{G}_P^{\delta} \qquad \text{(VIII – 14)}$$

$$\left(\frac{\partial \mu^{\delta}}{\partial T}\right)_P = -\overline{S}_P^{\delta} \qquad \text{(VIII – 15)}$$

$$\mu^{\delta} = \overline{X}_P^{\delta} - T\overline{S}_P^{\delta} \qquad \text{(VIII – 16)}$$

The corresponding relation equations against the assembly A that A_V, namely only one external parameter, is kept at constant are the relation equations in the special cases of the relation equations shown at the section of some functions of thermodynamics.[23] Namely, if suffix $\mathbb{V}$ is subscribed to indicate distinctly the condition of constant volume, the following equations, eq. (VIII – 17), eq. (VIII – 18), and eq. (VIII – 19), can be expressed respectively from three relations, $\mu^{\delta} = \overline{F}^{\delta}$, $\overline{S}^{\delta} = -\dfrac{\partial \mu^{\delta}}{\partial T}$ and $\mu^{\delta} = \overline{U}^{\delta} - T\overline{S}^{\delta}$, as

$$\mu^{\delta} = \overline{F}_V^{\delta} \qquad \text{(VIII – 17)}$$

$$\mu^{\delta} = \overline{U}_V^{\delta} - T\overline{S}_V^{\delta} \qquad \text{(VIII – 18)}$$

$$\left(\frac{\partial \mu^{\delta}}{\partial T}\right)_V = -\overline{S}_V^{\delta} \qquad \text{(VIII – 19)}$$

There are the following relations among the two kinds of partial molar quantity which are shown in these equations, from eq. (VIII –14) to eq. (VIII – 19).

The following equations, eq. (VIII – 20), eq. (VIII – 21), and eq. (VIII – 22), can be derived respectively from these relations,

$$\overline{G}_A^{\delta} = \overline{F}_A^{\delta} + P_A\overline{V}_A^{\delta},\ \overline{X}_A = \overline{U}_A^{\delta} + P_A\overline{\mathbb{V}}_A^{\delta},$$

and $\left(\frac{\partial \mu^{\delta}}{\partial P_A}\right)_T = \mathbb{V}_A^{\delta}$, as follows;

$$\overline{G}_P^{\delta} = \overline{F}_P^{\delta} + P\, \mathbb{V}_P^{\delta} \quad \text{(VIII – 20)}$$

$$\overline{X}_P^{\delta} = \overline{U}_P^{\delta} + P\, \mathbb{V}_P^{\delta} \quad \text{(VIII – 21)}$$

$$\left(\frac{\partial \mu^{\delta}}{\partial P}\right)_T = \mathbb{V}_P^{\delta} \quad \text{(VIII – 22)}$$

On the other hand, $\mathbb{P}^{\delta}$ of the assembly A_P which was proved on the previous paper,[23] μ^{δ} against A_V, and both eq. (VIII – 16) and eq. (VIII – 18) lead the following equation, eq. (VIII – 23).

$$\mu^{\delta} = \overline{X}_P^{\delta} - T\,\overline{S}_P^{\delta} = \overline{U}_V^{\delta} + T\overline{S}_V^{\delta} \quad \text{(VIII – 23)}$$

And, the following equation, eq. (VIII – 24) is derived from eq. (VIII – 15).

$$\overline{S}_P^{\delta} = -\left(\frac{\partial \mu^{\delta}}{\partial T}\right)_P = -\left(\frac{\partial \mu^{\delta}}{\partial T}\right)_V + \left(\frac{\partial \mu^{\delta}}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_V \quad \text{(VIII – 24)}$$

Or, according to these equations, eq. (VIII – 19), eq. (VIII – 22), and the following equation, eq. (VIII – 25), the following equation, eq. (VIII – 26), is derived.

$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{1}{\mathbb{V}}\left(\frac{\partial \mathbb{V}}{\partial T}\right)_P \Big/ \frac{1}{\mathbb{V}}\left(\frac{\partial \mathbb{V}}{\partial P}\right)_T \quad \text{(VIII – 25)}$$

$$\overline{S}_P^{\delta} = \overline{S}_V^{\delta} + \frac{\alpha}{\beta}\overline{\mathbb{V}}_P^{\delta} \quad \text{(VIII – 26)}$$

Here, the relation shown in the following equation, eq. (VIII – 27), or the relation shown in the following equation, eq. (VIII – 28), is expansion coefficent or compressibility coefficient respectively.

$$\alpha = \frac{1}{\mathbb{V}}\left(\frac{\partial \mathbb{V}}{\partial T}\right)_P \quad \text{(VIII – 27)}$$

and,

$$\beta = -\frac{1}{\mathbb{V}}\left(\frac{\partial \mathbb{V}}{\partial P}\right)_T \quad \text{(VIII – 28)}$$

Also, the following equations, eq. (VIII – 29) and eq. (VIII – 30), are derived from the equations, eq. (VIII –21), eq. (VIII – 23), and eq. (VIII – 26).

$$\overline{X}_P^{\delta} = \overline{U}_V^{\delta} + T\frac{\alpha}{\beta}\mathbb{V}_P^{\delta} \quad \text{(VIII – 29)}$$

and

$$\overline{\overline{U}}_P^{\delta} = \overline{U}_V^{\delta} + \left(T\frac{\alpha}{\beta} - P\right)\mathbb{V}_P^{\delta} \quad \text{(VIII – 30)}$$

Moreover, the following equation, eq. (VIII – 31) is derived from the equations, eq. (VIII – 15), eq. (VIII – 22), and eq. (VIII – 23).

$$\left(\frac{\partial \overline{X}_P^{\delta}}{\partial P}\right)_T = \mathbb{V}_P^{\delta} - T\left(\frac{\partial \overline{V}^{\delta}}{\partial T}\right)_P \quad \text{(VIII – 31)}$$

Discussion and Conclusion

As the pagination for one report is limited, then the centents must be shortened for this section. However, the important part cannot be shortened very much. Especially, the section of Experimental and Results is most important than other sections. So, it is reasonable that many paginations are used for it.

In regard to eq. (VIII – 6), the volume which is external parameter of part A must be constant against partial differentiation according to the condition that the general equation, $S = -\frac{\partial F}{\partial T}$, is assumed tacitly.

In regard to eq. (VIII – 7), if eq. (VIII – 6) is substituted in the identity, the following equation, eq. (VIII – A), the following equation, eq. (VIII – B), can be derived.

$$\left(\frac{\partial F_A}{\partial T}\right)_{P_A} = \left(\frac{\partial F_A}{\partial T'}\right)_{V_A} + \left(\frac{\partial F_A}{\partial V_A}\right)_T\left(\frac{\partial V_A}{\partial T}\right)_{P_A} \quad \text{(VIII – A)}$$

$$-S_A = \left(\frac{\partial F_A}{\partial T}\right)_{P_A} - \left(\frac{\partial V_A}{\partial T}\right)_{P_A} \quad \text{(VIII – B)}$$

Also, if the following equation, eq. (VIII – C), is differentiated, the following equation, eq. (VIII – D), can be derived.

$$G_A = F_A + P_A\mathbb{V}_A \quad \text{(VIII – C)}$$

$$\left(\frac{\partial G_A}{\partial T}\right)_{P_A} = \left(\frac{\partial F_A}{\partial T}\right)_{P_A} + P_A\left(\frac{\partial V_A}{\partial T}\right)_{P_A} \quad \text{(VIII – D)}$$

And, if the following equation, eq. (VIII – E), is substituted in eq. (VIII – D), the following equation, eq. (VIII – F), can be derived.

$$P_A = -\left(\frac{\partial F_A}{\partial V_A}\right)_T \quad \text{(VIII – E)}$$

$$\left(\frac{\partial G_A}{\partial T}\right)_{P_A} = \left(\frac{\partial F_A}{\partial T}\right)_{P_A} - \left(\frac{\partial F_A}{\partial V_A}\right)_T\left(\frac{\partial V_A}{\partial T}\right)_{P_A} \quad \text{(VIII – F)}$$

Thus, eq. (VIII – 7) can be derived. However, the suffix P_A of $\left(\frac{\partial G_A}{\partial T}\right)_{P_A}$ is not subscribed in eq. (VIII – 7).

In regard to eq. (VIII –24), the relation shown in the following equation, eq. (VIII – G), can be derived.

$$d\mu^\delta = \left(\frac{\partial \mu^\delta}{\partial T}\right)_P dT + \left(\frac{\partial \mu^\delta}{\partial P}\right)_T dP \quad \text{(VIII – G)}$$

Consequently, the relation shown in the following equation, eq. (VIII – H) can be derived.

$$\left(\frac{\partial \mu^\delta}{\partial T}\right)_V = \left(\frac{\partial \mu^\delta}{\partial T}\right)_P + \left(\frac{\partial \mu^\delta}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_V \quad \text{(VIII – H)}$$

In regard to eq. (VIII –25), the relation shown in the following equation, eq. (VIII – I), can be derived.

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV \quad \text{(VIII – I)}$$

Consequently, the relation shown in the following equation, eq. (VIII – J) can be derived.

$$O = \left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P \quad \text{(VIII – J)}$$

In regard to eq. (VIII – 31), the following equation, eq. (VIII – K) can be derived from eq. (VIII – 23).

$$\overline{X}_P^\delta = \mu^\delta + T\overline{S}_P^\delta \quad \text{(VIII – K)}$$

If the partial differentiation of eq. (VIII – K) is performed in regard to P, the relation shown in the following equation, eq. (VIII – L), can be derived.

$$\left(\frac{\partial \overline{X}_P^\delta}{\partial P}\right)_T = \left(\frac{\partial \mu^\delta}{\partial P}\right)_T + T\left(\frac{\partial \overline{S}_P^\delta}{\partial P}\right)_T \quad \text{(VIII – L)}$$

The relation shown in the following equation, eq. (VIII – M), can be derived from eq. (VIII – 15).

$$\overline{S}_P^\delta = -\left(\frac{\partial \mu^\delta}{\partial T}\right)_P \quad \text{(VIII – M)}$$

Consequently, the relation shown in the following equation, eq. (VIII – N) can be derived.

$$\left(\frac{\partial \overline{S}_P^\delta}{\partial P}\right)_T = -\frac{\partial^2 \mu^\delta}{\partial P \partial T} = -\left(\frac{\partial \overline{V}_P^\delta}{\partial T}\right)_P \quad \text{(VIII – N)}$$

If eq. (VIII – N) and eq. (VIII – 22) are substituted in the above described equation, eq. (VIII – L), the relation shown in the following equation, eq. (VIII – O), can be derived.

$$\left(\frac{\partial \overline{X}_P^\delta}{\partial P}\right)_T = \overline{V}_P^\delta - T\left(\frac{\partial \overline{V}_P^\delta}{\partial T}\right)_P \quad \text{(VIII – O)}$$

Namely, eq. (VIII – 31) can be obtained.

The several selected subjective points that must be understood in advance are considered as stated above.

Summary

The rest parts of theoretical treatments for both rest part of thermodynacial type of λ against the assembly A_P and rest part of thermodynamical type of the quantity led from it are considered and shown in on this paper.

References

1) L. Pauling, E. B. Wilson; *Introduction to Quantum Mechanics*, Mc GRAW-HILL, 1935, New York.
2) R. C. Tolman; *The Principles of Statistical Mechanics*, Oxford Univ. Press., 1938, Glasgow.
3) J. E. Mayer; *Statistical Mechanics*; John Wiley & Sons, 1940, New York.
4) A. I. Khinchin; *Mathematical Foundations of Statistical Mechanics*, Dover Pub., 1949, New York.

5) H. Goldstein; *Classical Mechanics*, Addison-Wesley Pub., 1950, London.
6) F. W. Sears; *Thermodynamics, the Kinetic Theory of Gases, and Statistical Mechanics*, Addison-Wesley Pub., 1953, Massachusetts.
7) L. I. Schiff; *Quantum Mechanics*, 3rd Ed. Inter. Stu. Ed., 1955, New York.
8) P. A. M. Dirac; *The Principles of Quantum Mechanics*, 4th Ed., Oxford Clarendon Press., 1958, Glasgow.
9) F. W. Sears; *Thermodynamics*, Addison-Wesley Pub., 1959, Massachusetts.
10) A. A. Frost, R. G. Pearson; *Kinetics and Mechanism*, John Wiley & Sons, 1961, New York.
11) E. Schrödinger; *Statstical Thermodynamics*, Cambridge Univ. Press., 1964, Cambridge.
12) R. P. Feynman, A. R. Hibbs; *Quantum Mechanics and Path Integrals*, Mc GRAW-HILL, 1965, New York.
13) T. C. Bradbury; *Theoretical Mechanics*, Wiley Inter. Ed., 1968, New York.
14) W. Miller, H. F. Schasfer, B. J. Berne, G. A. Segal; *Modern Theoretical Chemistry*, A. B. Prenum Press., 1977, New York.
15) D. R. Cox, P. A. W. Lewis; *The Statistical Analysis of Series of Events*, Chapman & Hall, 1978, London.
16) B. H. Lavenda; *Thermodynamics of Irreversible Processes*, Macmillan, 1978, London.
17) K. Baclawski, M. D. Donsker; Mark Kac: *Probability, Number Theory, and Statistical Physics*, Selected Papers, MIT Press., 1979, Cambridge.
18) K. Horitsu; Bull. Tokyo Kasei Daigaku, 23(2) 15 1983.
19) K. Horitsu; ibid., 23(2) 23 1983.
20) K. Horitsu; ibid., 24(2) 23 1984.
21) K. Horitsu; ibid., 24(2) 35 1984.
22) K. Horitsu; ibid., 25 119 1985.
23) K. Horitsu; ibid., 25 135 1985.
24) K. Horitsu, ibid., in press.

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

化学反応の理論的取扱
第8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，さらに発展させた。

集団Apに対するλの熱力学的型についての残された部分およびそれから導かれた量の熱力学的型の残された部分の両方に対する理論的取扱の残された部分を考察し，示した。