One Theoretical Treatment of Chemical Reaction Part11 : Reaction to Statistcal Mechanics for Homogeneous Fluid Partially

〔Bull. Tokyo Kasei University 33(2), P. 1 ~ 5, 1993〕

One Theoretical Treatment of Chemical Reaction
Part 11 Reaction to statistcal Mechanics for Homogeneous Fluid partially

Keisuke HORITSU

Laboratory of Biology

(Received October 1, 1992)

Introduction

This new theoretical treatment applied to liquid phase on the basis of gas phase like the previous paper[1~27] after the application to gas phase. And this theoretical treatment[28] is tried to extend furthermore over the previous paper[27]. Like the previous paper, a fuge lot of particle that is considered conceptually is substituted to a fuge lot of molecule. The concept that a particle imagines a molecule derives the replacement of gas phase against liquid phase. The number of molecule at liquid phase is very large in comparison with gas phase. And a very dilute solution approaches to gaseous state on the simular level with number of molecule. Of course, liquid phase is different from gas phase on other levels, for example interaction of solute molecule and solvent molecule, ion, ionic strength, dipole moment, electric force, and others.

Experimental and Results, Gedanken Experiment

On the fundamental consideration that $\bar{F}^{\delta}_{V,l}$, $\bar{F}^{\delta}_{P,l}$, and $\bar{G}_P$, were defined on the previous paper, $\bar{S}^{\delta}_{V,l}$ and $\bar{S}^{\delta}_{P,l}$ are defined like the following equations,

$$\bar{S}^{\delta}_{V,l} = \bar{S}^{\delta}_{V} + R \log \mathbb{N}^{\delta} \qquad \text{(XI-1)}$$

$$\bar{S}^{\delta}_{P,l} = \bar{S}^{\delta}_{P} + R \log \mathbb{N}^{\delta} \qquad \text{(XI-2)}$$

Laboratory of Biology

On the other hand, the partial differentiation of each μ^{δ} of equation (IX-16), $\mu^{\delta} = \mu^{\delta}_{l} + RT \log \mathbb{N}^{\delta}$ [26], is considered under the condition of constant volume or constant pressure against T. As the reaction, equation (X-23), $\mathbb{N}^{\delta} = n^{\delta} / \mathbb{V}$ [27] is considered, the following relations are derived.

$$\left(\frac{\partial \mu^{\delta}}{\partial T}\right)_V = \left(\frac{\partial \mu^{\delta}_{l}}{\partial T}\right)_V + R \log \mathbb{N}^{\delta} \qquad \text{(XI-3)}$$

$$\left(\frac{\partial \mu^{\delta}}{\partial T}\right)_P = \left(\frac{\partial \mu^{\delta}_{l}}{\partial T}\right)_P - RT\alpha + R \log \mathbb{N}^{\delta} \qquad \text{(XI-4)}$$

From the equations, (XI-1) and (XI-2), and the equations, $\left(\frac{\partial \mu^{\delta}}{\partial T}\right)_V = -\bar{S}^{\delta}_{V}$ (VIII-19)[25] and $\left(\frac{\partial \mu^{\delta}}{\partial T}\right)_P = -\bar{S}^{\delta}_{P}$ (VIII-15)[25], the equations, (XI-3) and (XI-4),

$$\bar{S}^{\delta}_{V,l} = -\left(\frac{\partial \mu^{\delta}_{l}}{\partial T}\right)_V \qquad \text{(XI-5)}$$

$$\bar{S}^{\delta}_{P,l} = -\left(\frac{\partial \mu^{\delta}_{l}}{\partial T}\right)_P + RT\alpha \qquad \text{(XI-6)}$$

From the equations, (XI-1) and (XI-2), and equations, $\bar{G}^{\delta}_{P} = \bar{F}^{\delta} + P\bar{\mathbb{V}}^{\delta}_{P}$ (VIII-20)[25], $\bar{X}^{\delta}_{P} = \bar{U}^{\delta}_{P} + P\bar{\mathbb{V}}^{\delta}_{P}$ (VIII-21)[25], $\left(\frac{\partial \mu^{\delta}}{\partial T}\right)_T = \bar{\mathbb{V}}^{\delta}_{P}$ (VIII-22)[25], $\mu^{\delta} = \bar{X}^{\delta}_{P}$

$-T\bar{S}_P^\delta = \bar{U}_V^\delta - T\bar{S}_V^\delta$ (VIII-23)[25], $\bar{S}_P^\delta = \bar{S}_V^\delta + \frac{\alpha}{\beta}\bar{V}_P^\delta$ (VIII-26)[25],

$$\bar{S}_{P,1}^\delta = \bar{S}_{V,1}^\delta + \frac{\alpha}{\beta}\bar{V}_P^\delta \quad \text{(XI-7)}$$

From the equations, $\mu^\delta = \bar{G}_P^\delta$ (VIII-14)[25], $\left(\frac{\partial\mu^\delta}{\partial T}\right)_P = -\bar{S}_V^\delta$ (VIII-15)[25], $\mu^\delta = \bar{X}_P^\delta - T\bar{S}_P^\delta$ (VIII-16)[25], $\mu^\delta = \bar{F}_V^\delta$ (VIII-17)[25], $\left(\frac{\partial\mu^\delta}{\partial T}\right)_V = -\bar{S}_V^\delta$ (VIII-18)[25], $\mu^\delta = \bar{U}_V^\delta - T\bar{S}_V^\delta$ (VIII-19)[25], $\bar{G}_P^\delta = \bar{F}_P^\delta + P\bar{V}_P^\delta$ (VIII-20)[25], $\bar{X}_P^\delta = \bar{U}_P^\delta + P\bar{V}_P^\delta$ (VIII-21)[25], $\left(\frac{\partial\mu^\delta}{\partial P}\right)_T = \bar{V}_P^\delta$ (VIII-22)[25], $\mu^\delta = \bar{X}_P^\delta - T\bar{S}_P^\delta = \bar{U}_V^\delta - T\bar{S}_V^\delta$ (VIII-23)[25], $\bar{S}_P^\delta = \bar{S}_V^\delta + \frac{\alpha}{\beta}\bar{V}_P^\delta$ (VIII-24)[25], the follwing equations for $\bar{U}_V^\delta$, $\bar{U}_P^\delta$ and $\bar{X}_P^\delta$ are derived.

$$\bar{U}_V^\delta = \bar{F}_V^\delta + T\bar{S}_V^\delta \quad \text{(XI-8)}$$

$$\bar{U}_P^\delta = \bar{X}_P^\delta - P\bar{V}_P^\delta \quad \text{(XI-9)}$$

$$\bar{X}_{P,1}^\delta = \bar{G}_P^\delta + T\bar{S}_{P,1}^\delta \quad \text{(XI-10)}$$

$\bar{U}_{V,1}^\delta$, $\bar{U}_{P,1}^\delta$. and $\bar{X}_{P,1}^\delta$ are defined corresponding to the equations, (XI-8), (XI-9), and (XI-10).

$$\bar{U}_{V,1}^\delta = \bar{F}_{V,1}^\delta + T\bar{S}_V^\delta \quad \text{(XI-11)}$$

$$\bar{U}_{P,1}^\delta = \bar{X}_{P,1}^\delta - P\bar{V}_P^\delta \quad \text{(XI-12)}$$

$$\bar{X}_{P,1}^\delta = \bar{G}_{P,1}^\delta + T\bar{S}_{P,1}^\delta \quad \text{(XI-13)}$$

From the equations, $\bar{F}_{V,1}^\delta = \bar{F}_V^\delta - RT\log N^\delta$ (X-15)[27], $\bar{F}_{P,1}^\delta = \bar{F}_P^\delta - RT\log N^\delta$ (X-16)[27], $\bar{G}_{P,1}^\delta = \bar{G}_P^\delta - RT\log N^\delta$ (X-17), (XI-5), (XI-6), (XI-8), (XI-9), (XI-10), (XI-11), (XI-12), and (XI-13), the following equations are dedived.

$$\bar{U}_{V,1}^\delta = \bar{U}_V^\delta \quad \text{(XI-14)}$$

$$\bar{U}_{P,1}^\delta = \bar{U}_P^\delta \quad \text{(XI-15)}$$

$$\bar{X}_{P,1}^\delta = \bar{X}_P^\delta \quad \text{(XI-16)}$$

Consequently, from $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ (VIII-27)[25], $\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_P$ (VIII-28)[25], $\bar{X}_P^\delta = \bar{U}_V^\delta + T\frac{\alpha}{\beta}\bar{V}_P^\delta$ (VIII-29)[25], $\bar{U}_P^\delta = \bar{U}_V^\delta + \left(T\frac{\alpha}{\beta} - P\right)\bar{V}_P^\delta$ (VIII-30)[25], $\left(\frac{\partial\bar{X}_P^\delta}{\partial P}\right)_T = \bar{V}_P^\delta - T\left(\frac{\partial\bar{V}_P^\delta}{\partial T}\right)_P$ (VIII-31)[25], the following equations are

$$\bar{X}_{P,1}^\delta = \bar{U}_{V,1}^\delta + T\frac{\alpha}{\beta}\bar{V}_P^\delta \quad \text{(XI-17)}$$

$$\bar{U}_{P,1}^\delta = \bar{U}_{V,1}^\delta + \left(T\frac{\alpha}{\beta} - P\right)\bar{V}_P^\delta \quad \text{(XI-18)}$$

$$\left(\frac{\partial\bar{X}_{P,1}^\delta}{\partial T}\right)_T = \bar{V}_P^\delta - T\left(\frac{\partial\bar{V}_P^\delta}{\partial T}\right)_P \quad \text{(XI-19)}$$

In an ideal solution, μ_1^μ $(=\mu^\delta)$ is constant under the conditions of constant volume and constant pressure in spite of N^δ. Then, if α and β are constant or if these changes of these quantities by N^δ are possible to neglect, the above described quantities with suffix 1 are constant in spite of N^δ.The above described results are concluded from the above described definitions and related equations. Generally, it is considered that these quantities with suffix 1 shows the properties of standard state. For example, the standard state is meaning to the ideal solution of $N^\delta = 1$. However, the consideration of ideal solution is not fixed here. These quantities should be treated as the showing of the properties of the objective solution itself, even the solution is ideal or not.

In the case of gas, $PV = \sum_{i=o}^{i=s} n^{\delta i}RT$(X-13)[27] derives the following relations,

$$\alpha = \frac{1}{T} \quad \text{(XI-20)}$$

$$\beta = \frac{1}{P} \quad \text{(XI-21)}$$

$$\bar{V}_P^\delta = \frac{RT}{P} \quad \text{(XI-22)}$$

These quantities are not related to $\mathbb{N}^{\delta}$ strictly speaking. In this case, $\mu_{l}^{\delta} = \bar{F}_{V,l}^{\delta} = \bar{F}_{P,l}^{\delta} + P\bar{V}_{P}^{\delta} = \bar{G}_{P,l}^{\delta}$ (X-22)[27], $\mathbb{N}^{\delta} = n^{\delta}/\mathbb{V}$ (X-23)[27], $\left(\frac{\partial \bar{F}_{V,l}^{\delta}}{\partial P}\right)_T = \left(\frac{\partial \bar{G}_{P,l}^{\delta}}{\partial P}\right)_T = \bar{V}_{P}^{\delta} - RT\beta$ (X-23)[27], the equations, (XI-5), (XI-6), (XI-7), (XI-11), (XI-12), (XI-13), (XI-17), (XI-18), and (XI-19), are deformed to the following special forms.

$$\mu^{\delta} = \bar{F}_{V,l}^{\delta} = \bar{F}_{P,l}^{\delta} + RT = \bar{G}_{P,l}^{\delta} \quad \text{(XI-23)}$$

$$\bar{S}_{V,l}^{\delta} = -\left(\frac{\partial \mu_{l}^{\delta}}{\partial T}\right)_V = \bar{S}_{P,l}^{\delta} - R = -\left(\frac{\partial \mu_{l}^{\delta}}{\partial T}\right)_P \quad \text{(XI-24)}$$

$$\bar{U}_{V,l}^{\delta} = \bar{U}_{P,l}^{\delta} = \bar{X}_{P,l}^{\delta} - RT \quad \text{(XI-25)}$$

$$\left(\frac{\partial X_{P,l}^{\delta}}{\partial P}\right)_T = 0 \quad \text{(XI-26)}$$

Discussion and Conclusion

The fundamental concept of this new theoretical treatment is on the base of statistical mechanics, quantum mechanics, and thermodynamics for this wide application. This consideration is possible to apply to a biological reaction. Of course, this scientific consideration must support much analysis and understanding with respect to various complicated problems of living matter which is one final object.

Then, the extension of the theoretical treatment was tried to several definitions, $\bar{S}_{V,l}^{\delta}$, and $\bar{S}_{P,l}^{\delta}$. And μ^{δ} was differentiated with respect to temperature under constant volume and constant pressure. Moreover, $\bar{S}_{V,l}^{\delta}$ and $\bar{S}_{P,l}^{\delta}$ was treated with the relation of differentiated μ^{δ}/T against constant volume and constant pressure. Also, the relation between $\bar{S}_{V,l}^{\delta}$ and $\bar{S}_{P,l}^{\delta}$ induced the $\bar{V}_{P}^{\delta}$ and the factor of α to β.

Moreover, $\bar{U}_{V}^{\delta}$, $\bar{U}_{P}^{\delta}$ and $\bar{X}_{P}^{\delta}$ were defined with respect to $\bar{F}_{V}^{\delta}$, T and $\bar{S}_{V}^{\delta}$, $\bar{X}_{P}^{\delta}$, P and $\bar{V}_{P}^{\delta}$, and $\bar{G}_{P}^{\delta}$, T and $\bar{S}_{P}^{\delta}$ respectively. Also, the condition of fixing to V and P extended to V, l and P, l respectively understanding the analysis of practical phenomenon easily. Therefore, the relation between suffix V, l and suffix V was clearified. And the relation of $\bar{X}_{P,l}^{\delta}$, $\bar{U}_{V,l}^{\delta}$, T, α and β , $\bar{V}_{P}^{\delta}$, the relation of $\bar{U}_{P,l}^{\delta}$, $\bar{U}_{V,l}^{\delta}$, T, α and β , P, $\bar{V}_{P}^{\delta}$, and the relation of $\partial \bar{X}_{P,l}^{\delta}/\partial P$ at constant temperature, $\bar{V}_{P}^{\delta}$, T, $\partial \bar{V}_{P}^{\delta}/\partial T$ at constant pressure were clearified respectively to approach to real phenomenon.

The case of ideal solution was considered the condition that μ_{l}^{δ} $(=\mu^{\delta})$ was constant at constant temperature and constant pressure regardless of $\mathbb{N}^{\delta}$. So, if α and β was constant respectively or if the change of the quantity depended upon $\mathbb{N}^{\delta}$ was neglected, the quantities fixed with suffix l became constant regardlss of $\mathbb{N}^{\delta}$. These conclusions were derived by these above described definitions and related equations. This suffix l meaned the property at standard state that was ideal solution of $\mathbb{N}^{\delta} = l$. Generally, an ideal condition is considered as a basic condition that the various factors in real phenomenon is made to minimize. Really, the ideal concept that such a standard state was assumed as an ideal solution had to develope to the properties of the real problem. This point is one important objective to solute the complicated real condition. Such a solution must be treated by this new theoretical treatment. Also, this application is one of the final object.

And, in the case of gas, $\alpha = l/T$, $\beta = l/P$, $\bar{V}_{P}^{\delta} = RT/P$ is valid respectively. These quantities are dependent on $\mathbb{N}^{\delta}$ strictly.

μ^{δ} is equal to $\bar{F}_{V,l}^{\delta}$, $\bar{F}_{P,l}^{\delta} + RT$, or $\bar{G}_{P,l}^{\delta}$. And $\bar{S}_{V,l}^{\delta}$ is equal to $\bar{U}_{P,l}^{\delta}$, or $\bar{X}_{P,l}^{\delta} - RT$. Moreover, $(\partial \bar{X}_{P,l}^{\delta}/\partial P)$ at fixation of l is equal to 0. These typical forms were the fundermental typical forms to solute the complicated practical problems.

On the other hand, from $\bar{F}_{V,l}^{\delta}$, $\left(\frac{\partial \bar{F}_{V,l}^{\delta}}{\partial P}\right)_T$, and $\left(\frac{\partial \bar{F}_{V,l}^{\delta}}{\partial P}\right)_T = \left(\frac{\partial \bar{G}_{P,l}^{\delta}}{\partial P}\right)_T = \bar{V}_{P}^{\delta} - RT\beta$ (X-24), $\bar{V}_{P}^{\delta}$ is constant in spite of $\mathbb{N}^{\delta}$. Therefore, the simular conclusion is derived against all quantities with suffix l from other related equations.

Summary

On this paper, the concept of ideal solution was tried to apply to one real condition. The consideration that this new theoretical treatment is possible to apply to a real chemical reaction is showed as one example.

$\bar{S}_{V,l}^{\delta}$ and $\bar{S}_{P,l}^{\delta}$ were defined. And $(\partial \mu^{\delta}/\partial T)_V$ and

$(\partial \mu^{\delta} / \partial T)_P$ were showed in the relation to $\mathbb{N}^{\delta}$, R, and T.

Furthermore, it was showed that the relation among $\bar{S}^{\delta}_{V,I}$ and $\bar{S}^{\delta}_{P,I}$, and $(\partial \mu^{\delta} / \partial T)_V$ and $(\partial \mu^{\delta} / \partial T) + RT\alpha$. And $\bar{S}^{\delta}_{P,I}$ was related to $\bar{S}^{\delta}_{V,I}$ and $\alpha / T\ \bar{\mathbb{V}}^{\delta}_P$.

Also, $\bar{U}^{\delta}_V$, $\bar{U}^{\delta}_P$, and $\bar{X}^{\delta}_P$ were related to $\bar{F}^{\delta}_V + T\bar{S}^{\delta}_V$, $\bar{X}^{\delta}_P - P\bar{\mathbb{V}}^{\delta}_P$ and $\bar{G}^{\delta}_P + T\bar{S}^{\delta}_P$ respectively. Moreover, after one part of description was neglectful of the detailed description, it was showed that $\bar{U}^{\delta}_{V,I}$, $\bar{U}^{\delta}_{P,I}$, and $\bar{X}^{\delta}_{P,I}$ were related to $\bar{U}^{\delta}_V$, $\bar{U}^{\delta}_P$, and $\bar{X}^{\delta}_P$ respectively. And $\bar{X}^{\delta}_{P,I}$, $\bar{U}^{\delta}_{P,I}$, and $(\partial \bar{X}^{\delta}_{P,I} / \partial P)_T$ were showed. Furthermore, one ideal condition was tried to one real condition. It was very important to develope this new theoretical treatment.

And it was showed this important relations that (a) : μ^{δ}, (b) : $\bar{S}^{\delta}_{V,I}$, (c) : $\bar{U}^{\delta}_{V,I}$, and (d) : $(\partial \bar{X}^{\delta}_{P,I} / \partial P)_T$ were equal to (a) : $\bar{F}^{\delta}_{V,I}$, $\bar{F}^{\delta}_{P,I} + RT$, and $\bar{G}^{\delta}_{P,I}$, (b) : $-(\partial \mu^{\delta}_I / \partial T)_V$, $\bar{S}^{\delta}_{P,I} - R$, and $-(\partial \mu^{\delta}_I / \partial T)_P$, (c) : $\bar{U}^{\delta}_{P,I}$, and $\bar{X}^{\delta}_{P,I} - RT$, and (d) : 0 respectively having each special form.

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-Wesly Pub. London
6) F. W. Sears: Thermodynamics, the Kinetic Theory of Gases, and Statistical Mechanics, Addison-Wesley Pub., 1953, Masachusetts
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. Schrodinger: Statistical Thermodynamics, Cambridge Univ. Press., 1964, Cambridge
12) R. P. Feynman, A. R. Hibbs: Quantum Mechanics and 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, 1878, London
16) B. H. Lavende: Thermodynamics of Irreversible Process, 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., 26 123 1986
25) K. Horitsu: ibid., 26 127 1986
26) K. Horitsu: Bull. Tokyo Kasei Univ. 29 111 1989
27) K. Horitsu: ibid., 31 1 1991
28) 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 experimental and results (Gedanken Experiment) should be shortened in that order. The rigorous restriction was one person one contribution one year.

化学反応の理論的取扱

第11報　均一流体に対する統計力学一部との関係

堀　津　圭　佑

(平成 4 年 9 月28日受理)

本報で、理想溶液の思考は一つの実際の条件に応用するべく試みられた。この新しい理論的取扱は実際の化学反応に応用が可能であるという思考が一つの例として示されている。$\bar{S}^{\delta}_{V.I}$ と $\bar{S}^{\delta}_{P.I}$ が定義された。そして $(\partial\mu^{\delta}/\partial T)_V$ と $(\partial\mu^{\delta}/\partial T)_P$ は $\mathbb{N}^{\delta}$, R, と T との関係が示された。さらに $\bar{S}^{\delta}_{V.I}$ と $\bar{S}^{\delta}_{P.I}$ と $(\partial\mu^{\delta}/\partial T)_V$ と $(\partial\mu^{\delta}/\partial T)_P + RT\alpha$ との関係が示された。そして $\bar{S}^{\delta}_{P.I}$ は $\bar{S}^{\delta}_{V.I}$ と $(\alpha/T)\,\bar{\mathbb{V}}^{\delta}_P$ に関係づけられた。

また、$\bar{U}^{\delta}_V$, $\bar{U}^{\delta}_P$ と $\bar{X}^{\delta}_P$ はそれぞれ $\bar{F}^{\delta}_V + T\bar{S}^{\delta}_V$, $\bar{X}^{\delta}_P - P\bar{\mathbb{V}}^{\delta}_P$ と $\bar{G}^{\delta}_P + T\bar{S}^{\delta}_P$ に関係づけられた。さらに、記述の一部がその詳しい記述を無視された後、$\bar{U}^{\delta}_{V.I}$, $\bar{U}^{\delta}_{P.I}$ と $\bar{X}^{\delta}_{P.I}$ が $\bar{U}^{\delta}_V$, $\bar{U}^{\delta}_P$ と $\bar{X}^{\delta}_P$ にそれぞれ関係づけられたということを示した。そして、$\bar{X}^{\delta}_{P.I}$, $\bar{U}^{\delta}_{P.I}$ と $(\partial\bar{X}^{\delta}_{P.I}/\partial P)_T$ が示された。

さらに、一つの理想条件の思考が一つの実際の条件に試みられた。これはこの新しい理論的取扱を展開するのに非常に重要であった。

そして (a) : μ^{δ}, (b) : $\bar{S}^{\delta}_{V.I}$, (c) : $\bar{U}^{\delta}_{V.I}$ と (d) : $(\partial\bar{X}^{\delta}_{P.I}/\partial P)_T$ が (a) : $\bar{F}^{\delta}_{V.I}$, $\bar{F}^{\delta}_{P.I} - RT$, と $\bar{G}^{\delta}_{P.I}$, (b) : $-(\partial\mu^{\delta}_I/\partial T)_V$, $\bar{S}^{\delta}_{P.I} - R$, と $-(\partial\mu^{\delta}_I/\partial T)_P$, (c) : $\bar{U}^{\delta}_{P.I}$, $\bar{X}^{\delta}_{P.I} - RT$ と (d) : 0 とそれぞれ各各の特別の形をもって等しいというこの重要な関係が示された。