

One Theoretical Treatment of Chemical Reaction

Part 11 Reaction to statistical Mechanics for Homogeneous Fluid partially

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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 treatment²⁸⁾ is tried to extend furthermore over the previous paper²⁷⁾. 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 similar 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 $\bar{F}_{v,l}^\delta$, $\bar{F}_{p,l}^\delta$, and \bar{G}_p , were defined on the previous paper, $\bar{S}_{v,l}^\delta$ and $\bar{S}_{p,l}^\delta$ are defined like the following equations,

$$\bar{S}_{v,l}^\delta = \bar{S}_v^\delta + R \log N^\delta \quad (\text{XI-1})$$

$$\bar{S}_{p,l}^\delta = \bar{S}_p^\delta + R \log N^\delta \quad (\text{XI-2})$$

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

$$\left(\frac{\partial \mu^\delta}{\partial T} \right)_v = \left(\frac{\partial \mu_l^\delta}{\partial T} \right)_v + R \log N^\delta \quad (\text{XI-3})$$

$$\left(\frac{\partial \mu^\delta}{\partial T} \right)_p = \left(\frac{\partial \mu_l^\delta}{\partial T} \right)_p - RT\alpha + R \log N^\delta \quad (\text{XI-4})$$

From the equations, (XI-1) and (XI-2), and the equations, $\left(\frac{\partial \mu^\delta}{\partial T} \right)_v = -\bar{S}_v^\delta$ (VIII-19)²⁵⁾ and $\left(\frac{\partial \mu^\delta}{\partial T} \right)_p = -\bar{S}_p^\delta$ (VIII-15)²⁵⁾, the equations, (XI-3) and (XI-4),

$$\bar{S}_{v,l}^\delta = - \left(\frac{\partial \mu_l^\delta}{\partial T} \right)_v \quad (\text{XI-5})$$

$$\bar{S}_{p,l}^\delta = - \left(\frac{\partial \mu_l^\delta}{\partial T} \right)_p + RT\alpha \quad (\text{XI-6})$$

From the equations, (XI-1) and (XI-2), and equations,

$$\bar{G}_p^\delta = \bar{F}^\delta + P \bar{V}_p^\delta \quad (\text{VIII-20})^{25)}, \bar{X}_p^\delta = \bar{U}_p^\delta + P \bar{V}_p^\delta$$

$$(\text{VIII-21})^{25)}, \left(\frac{\partial \mu^\delta}{\partial T} \right)_T = \bar{V}_p^\delta \quad (\text{VIII-22})^{25)}, \mu^\delta = \bar{X}_p^\delta$$

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

$$\text{(VIII-26)}^{25)},$$

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

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

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

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

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

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

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

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

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

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

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

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

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

Consequently, from $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \text{ (VIII-27)}^{25)},$

$$\beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_P \text{ (VIII-28)}^{25)}, \bar{X}_P^\delta = \bar{U}_V^\delta + T\frac{\alpha}{\beta} \bar{V}_P^\delta$$

$$\text{(VIII-29)}^{25)}, \bar{U}_P^\delta = \bar{U}_V^\delta + \left(T\frac{\alpha}{\beta} - P \right) \bar{V}_P^\delta \text{ (VIII-30)}^{25)},$$

$$\left(\frac{\partial \bar{X}_P^\delta}{\partial P} \right)_T = \bar{V}_P^\delta - T \left(\frac{\partial \bar{V}_P^\delta}{\partial T} \right)_P \text{ (VIII-31)}^{25)},$$
 the following

equations are

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

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

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

In an ideal solution, $\mu_1^\mu (= \mu^\delta)$ 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 chan-
 ges of these quantities by N^δ are possible to neglect, the
 above described quantities with suffix l 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 l 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, $PV = \sum_{i=0}^{i=s} n^{\delta i} RT \text{ (X-13)}^{27)}$ 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 N^δ strictly speaking. In this case, $\mu_i^\delta = \bar{F}_{V,i}^\delta = \bar{F}_{P,i}^\delta + P \bar{V}_P^\delta = \bar{G}_{P,i}^\delta$ (X-22)²⁷⁾,

$$N^\delta = n^\delta / V \text{ (X-23)}^{27)}, \left(\frac{\partial \bar{F}_{V,i}^\delta}{\partial P} \right)_T = \left(\frac{\partial \bar{G}_{P,i}^\delta}{\partial P} \right)_T =$$

$\bar{V}_P^\delta - RT\beta$ (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.

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

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

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

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

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

Moreover, \bar{U}_V^δ , \bar{U}_P^δ and \bar{X}_P^δ were defined with respect to \bar{F}_V^δ , T and \bar{S}_V^δ , \bar{X}_P^δ , P and \bar{V}_P^δ , and \bar{G}_P^δ , T and \bar{S}_P^δ respectively. Also, the condition of fixing to V and P extended to V, I and P, I respectively understanding the analysis of practical phenomenon easily. Therefore, the relation between suffix V, I and suffix V was clarified. And the relation of $\bar{X}_{P,i}^\delta$, $\bar{U}_{V,i}^\delta$, T , α and β , \bar{V}_P^δ , the relation of $\bar{U}_{P,i}^\delta$, $\bar{U}_{V,i}^\delta$, T , α and β , P , \bar{V}_P^δ , and the relation

of $\partial \bar{X}_{P,i}^\delta / \partial P$ at constant temperature, \bar{V}_P^δ , T , $\partial \bar{V}_P^\delta / \partial T$ at constant pressure were clarified respectively to approach to real phenomenon.

The case of ideal solution was considered the condition that $\mu_i^\delta (= \mu^\delta)$ was constant at constant temperature and constant pressure regardless of N^δ . So, if α and β was constant respectively or if the change of the quantity depended upon N^δ was neglected, the quantities fixed with suffix I became constant regardless of N^δ . These conclusions were derived by these above described definitions and related equations. This suffix I meant the property at standard state that was ideal solution of $N^\delta = I$. 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 develop to the properties of the real problem. This point is one important objective to solve 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, $\alpha = 1/T$, $\beta = 1/P$, $\bar{V}_P^\delta = RT/P$ is valid respectively. These quantities are dependent on N^δ strictly.

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

$$\text{On the other hand, from } \bar{F}_{V,i}^\delta, \left(\frac{\partial \bar{F}_{V,i}^\delta}{\partial P} \right)_T, \text{ and } \left(\frac{\partial \bar{F}_{V,i}^\delta}{\partial P} \right)_T = \left(\frac{\partial \bar{G}_{P,i}^\delta}{\partial P} \right)_T = \bar{V}_P^\delta - RT\beta \text{ (X-24), } \bar{V}_P^\delta \text{ is constant in spite}$$

of N^δ . Therefore, the similar conclusion is derived against all quantities with suffix I 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.

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

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

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

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

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

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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 (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

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(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。 $\bar{S}_{V,I}^{\delta}$ と $\bar{S}_{P,I}^{\delta}$ が定義された。そして $(\partial\mu^{\delta}/\partial T)_V$ と $(\partial\mu^{\delta}/\partial T)_P$ は M^{δ} , R , と T との関係が示された。さらに $\bar{S}_{V,I}^{\delta}$ と $\bar{S}_{P,I}^{\delta}$ 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 $\bar{S}_{P,I}^{\delta}$ は $\bar{S}_{V,I}^{\delta}$ と $(\alpha/T) \bar{W}_P^{\delta}$ に関係づけられた。

また、 \bar{U}_V^{δ} , \bar{U}_P^{δ} と \bar{X}_P^{δ} はそれぞれ $\bar{F}_V^{\delta} + T\bar{S}_V^{\delta}$, $\bar{X}_P^{\delta} - P\bar{W}_P^{\delta}$ と $\bar{G}_P^{\delta} + T\bar{S}_P^{\delta}$ 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、 $\bar{U}_{V,I}^{\delta}$, $\bar{U}_{P,I}^{\delta}$ と $\bar{X}_{P,I}^{\delta}$ が \bar{U}_V^{δ} , \bar{U}_P^{δ} と \bar{X}_P^{δ} にそれぞれ関係づけられたということを示した。そして、 $\bar{X}_{P,I}^{\delta}$, $\bar{U}_{P,I}^{\delta}$ と $(\partial\bar{X}_{P,I}^{\delta}/\partial P)_T$ 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): $\bar{S}_{V,I}^{\delta}$, (c): $\bar{U}_{V,I}^{\delta}$ と (d): $(\partial\bar{X}_{P,I}^{\delta}/\partial P)_T$ が (a): $\bar{F}_{V,I}^{\delta}$, $\bar{F}_{P,I}^{\delta} - RT$, と $\bar{G}_{P,I}^{\delta}$, (b): $-(\partial\mu_I^{\delta}/\partial T)_V$, $\bar{S}_{P,I}^{\delta} - R$, と $-(\partial\mu_I^{\delta}/\partial T)_P$, (c): $\bar{U}_{P,I}^{\delta}$, $\bar{X}_{P,I}^{\delta} - RT$ と (d): 0 とそれぞれ各々の特別な形をもって等しいというこの重要な関係が示された。