One Theoretical Treatment of Chemical Reaction
Part 10　Relation to Statistical Mechanics for Homogeneous Fluid Partially

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Introduction

The new theoretical treatment applied to liquid phase from gaseous phase was published on the previous paper partially. Then, the theoretical treatment is tried to be extended furthermore on this paper partially[1~27].

A fuge lot of particle that is considered conceptually is substituted to a fuge lot of molecule. Such a conceptual substitution is not precise rigorously, but it avails the understanding of complicated system.

Experimental and Results, Gedanken Experiment

According to the following three equations, eq. (X-1), eq. (X-2), and eq. (X-3), that were published on the previous paper[26], the following relation showed as the following equation, eq. (X-4), is obtained.

$$\mathbb{V}_A\left(\frac{\partial P_A}{\partial \mathbb{V}_A}\right)_T = n^{\delta_0}\left(\frac{\partial \mu^{\delta_0}}{\partial \mathbb{V}_A}\right)_T \tag{X-1}$$

$$\left(\frac{\partial \mu^{\delta_0}}{\partial \mathbb{V}_A}\right)_T = \left(\frac{\partial \mu_1^{\delta_0}}{\partial P_A}\right)_T\left(\frac{\partial P_A}{\partial \mathbb{V}_A}\right)_T - \frac{RT}{\mathbb{V}_A} \tag{X-2}$$

$$\left(\frac{\partial \mu^{\delta_0}}{\partial P_A}\right)_T = \overline{\mathbb{V}}^{\,\delta_0} = \left(\frac{\partial \mu_1^{\delta_0}}{\partial P_A}\right)_T + RT\beta_A \tag{X-3}$$

$$\left(\frac{\partial P_A}{\partial \mathbb{V}_A}\right)_T = \frac{n^{\delta_0}RT}{\mathbb{V}_A\{\mathbb{V}_A - n^{\delta_0}\overline{\mathbb{V}}^{\,\delta_0} + n^{\delta_0}RT\beta_A\}} \tag{X-4}$$

Then, the equation, eq. (X-4), is integrated. So, as P_A is equal to P_B, $P_A = P_B$, in the case that $\mathbb{V}_A$ is infinite, $\mathbb{V}_A = \infty$, the following relation showed as the following equation, eq. (X-5), is obtained.

$$\Pi^{\delta_0} = P_A - P_B = n^{\delta_0}RT\int_{\mathbb{V}_A}^{\infty}\frac{d\mathbb{V}_A}{\mathbb{V}_A\{\mathbb{V}_A - n^{\delta_0}\overline{\mathbb{V}}^{\,\delta_0} + n^{\delta_0}RT\beta_A\}}. \tag{X-5}$$

If $n^{\delta_0}RT\beta_A$ can be neglected in comparison with $\mathbb{V}_A - n^{\delta_0}\overline{\mathbb{V}}_P^{\,\delta_0}$, and if $\overline{\mathbb{V}}_P^{\,\delta_0}$ is constant and independent of $\mathbb{V}_A$, the equation, eq. (X-5), is rewritten as the following equation, eq. (X-6), in the relation that $\mathbb{N}^{\delta_0}$ is equal to $n^{\delta_0}/\mathbb{V}_A$, $\mathbb{N}^{\delta_0} = n^{\delta_0}/\mathbb{V}_A$.

$$\Pi^{\delta} = -\frac{RT}{\overline{\mathbb{V}}_P^{\,\delta_0}}\log(1 - \mathbb{N}^{\delta_0}\overline{\mathbb{V}}_P^{\,\delta_0}) \tag{X-6}$$

For example, a colloidal solution corresponds to such a case. In this case, $n^{\delta_0}\overline{\mathbb{V}}_P^{\,\delta_0}$ is volume occupied with colloidal particle in the solution. Then, as the determined value of Π^{δ_0} at various concentration is analyzed by the equation, eq. (X-6), the molecular weight of colloidal particle and the volume $\overline{\mathbb{V}}_P^{\,\delta_0}$ occupied with 1 mole can be determined at the same time.

If $n^{\delta_0}\overline{\mathbb{V}}_P^{\,\delta_0} - n^{\delta_0}RT\beta_A$ is small negligibly in comparison with $\mathbb{V}_A$, the equation, eq. (X-5), can be represented by the following equation, eq. (X-7).

$$\Pi^{\delta_0} = n^{\delta_0}\frac{RT}{\mathbb{V}_A} \tag{X-7}$$

Then, the following design was published on the previous paper. Namely, is one volume, A that is constituted with δ_0, δ_1, ..., δ_s divides B with a semipermeable membrane. But, B is constituted with δ_1, ..., δ_s. Now, if several ideal components, δ_0, ..., δ_t, that can not pass through the semipermeable membrane are existed in part A at the same time, instead of eq. (X-5), the following relation showed as the following equation, eq. (X-8), is

obtained with the similar reasoning as the above described case.

$$\Pi = \sum_{i=1}^{t} n^{\delta i} RT \int_{V_A}^{\infty} \frac{d V_A}{V_A \{V_A - \sum_{i=0}^{i=t} n_i^{\delta i}(V_P^{\delta_0} - RT\beta_A)\}} \quad (\text{X-8})$$

Moreover, if $\sum_{i=0}^{t} n^{\delta i}(\overline{V}_P^{\delta i} - RT\beta_A)$ is small negligibly in comparison with $\overline{V}_A$, the relation is rewritten as the following equation, eq. (X-9).

$$\Pi = \sum_{i=0}^{t} n^{\delta_i} \frac{RT}{V_A} \quad (\text{X-9})$$

In the case of gas, as the assembly is ideal respecting all component δ_i, all δ_i is independent of pressure. Consequently, this relation, $(\partial\mu_1^{\delta i}/\partial P)_T = 0$, is obtained by means of the following equation, eq. (X-10), published on the previous paper.

$$\mu_1^\delta = -RT \log Q^\delta \quad (\text{X-10})$$

Therefore, the following equation, eq. (X-11), is obtained from the following equation, eq. (X-12), published on the previous paper [26].

$$RT\beta - \overline{V}_P^{\delta i} = 0, \quad i = 0, 1, \cdots, S \quad (\text{X-11})$$

$$\left(\frac{\partial\mu^{\delta_0}}{\partial P_A}\right)_T = \overline{V}^{\delta_0} = \left(\frac{\partial\mu_1^{\delta_0}}{\partial P_A}\right)_T + RT\beta_A \quad (\text{X-12})$$

So, the relation showed by eq. (X-9) is valid. In this case, moreover, on the basis of the relation, $P_B = 0$, $\Pi = P_A$, if suffix A is eliminated, the relation showed as the following equation, eq. (X-13), is obtained.

$$P V = \sum_{i=0}^{i=S} n^{\delta i} RT \quad (\text{X-13})$$

Namely, thus the law of ideal gas is obtained. And, from the equation, eq. (X-13), the relation showed as the following equation, eq. (X-14), is obtained.

$$\beta = -\left(\frac{\partial \log V}{\partial P}\right)_T = \frac{1}{P} \quad \text{and} \quad V_P^{\delta i} = \frac{RT}{P} \quad (\text{X-14})$$

In consequence, the relation showed as eq. (X-11) is obtained reversely.

For a general homogenous fluid, $\overline{F}_{V,1}^\delta$, $\overline{F}_{P,1}^\delta$, and $\overline{G}_{P,1}^\delta$, are defined by the following relations showed as the following equations, eq. (X-15), eq. (X-16), and eq. (X-17), respectively.

$$\overline{F}_{V,1}^\delta = \overline{F}_V^\delta - RT \log N^\delta \quad (\text{X-15})$$

$$\overline{F}_{P,1}^\delta = \overline{F}_P^\delta - RT \log N^\delta \quad (\text{X-16})$$

$$\overline{G}_{P,1}^\delta = \overline{G}_P^\delta - RT \log N^\delta \quad (\text{X-17})$$

From the equations, eq. (X-15), eq. (X-16) and eq. (X-17), and the following equations showed on the previous papers, eq. (X-18), eq. (X-19), eq. (X-20), and eq. (X-21), the following relation showed as the following equation, eq. (X-22), is obtained.

$$\mu^\delta = \mu_1^\delta + RT \log N^\delta \quad (\text{X-18})$$

$$\mu^\delta = \overline{F}_V^\delta \quad (\text{X-19})$$

$$\mu^\delta = \overline{G}_P^\delta \quad (\text{X-20})$$

$$\overline{G}_P^\delta = \overline{F}_P^\delta + P \overline{V}_P^\delta \quad (\text{X-21})$$

$$\mu_1^\delta = \overline{F}_{V,1}^\delta = \overline{F}_{P,1}^\delta + P \overline{V}_P^\delta = \overline{G}_{P,1}^\delta \quad (\text{X-22})$$

Moreover, if the following relation showed as the following equation, eq. (X-23), is considered, the following equation, eq. (X-24), is concluded directly from the equations, eq. (X-15), eq. (X-16), eq. (X-17), and eq. (X-22), and the following equation, eq. (X-25), showed on the previous paper.

$$N^\delta = n^\delta / V \quad (\text{X-23})$$

$$\left(\frac{\partial\overline{F}_{V,1}^\delta}{\partial P}\right)_T = \left(\frac{\partial\overline{G}_{P,1}^\delta}{\partial P}\right)_T = \overline{V}_P^\delta - RT\beta \quad (\text{X-24})$$

$$\left(\frac{\partial\mu^\delta}{\partial P}\right)_T = \overline{V}_P^\delta \quad (\text{X-25})$$

Discussion and Conclusion

This theoretical treatment that was performed for the gaseous phase was applied to the homogeneous liquid phase at this step. When the number of particle in the gaseous phase increases to huge number, it is considered that one form becomes the liquid, and other form becomes the pressed gas. This point is one basis of this consideration. One part of this application was published on the previous paper [26]. But the residual part that the particle is exchanged to the molecule or the component is published on this paper. Also, the liquid is limited to the

homogenous liquid that the treatment is comparatively simple. Moreover, the heterogenous liquid may be published on other paper. The homogeneous liquid phase that the related molecules were divided with a semipermeable membrane in the decided volume was treated like the published case. Of course, the theoretical treatment and the consideration are based mainly on statistical mechanics and thermodynamics like the previous paper.

Some relations that help the understanding and the development of this new theoretical treatment are showed as the following descriptions.

The equation, eq. (X-6), was led, after the following relations showed as the following equation, eq. (X-I), were considered. Namely,

$$n^{\delta_0}RT\int_{V_A}^{\infty}\frac{dV_A}{V_A\,(V_A-n^{\delta_0}\bar{V}_P^{\delta_0})}$$

$$=\frac{n^{\delta_0}RT}{n^{\delta_0}\bar{V}_P^{\delta_0}}\left\{\int_{V_A}^{\infty}\frac{dV_A}{V_A-n^{\delta_0}\bar{V}_P^{\delta_0}}-\int_{V_A}^{\infty}\frac{dV_A}{V_A}\right\}$$

$$=\frac{RT}{\bar{V}_P^{\delta_0}}\log\frac{V_A}{V_A-n^{\delta_0}\bar{V}_P^{\delta_0}}-\lim_{V_A\to\infty}\log\frac{V_A}{V_A-n^{\delta_0}\bar{V}_P^{\delta_0}}$$

$$=\frac{RT}{\bar{V}_P^{\delta_0}}\log\frac{V_A}{V_A-n^{\delta_0}\bar{V}_P^{\delta_0}}\qquad\text{(X-I)}$$

Next, it is considered that the assembly is ideal respecting each component of the whole one. If such a limitation related to the assembly is not proposed, the development of this theoretical treatment must become more complicate and more difficult. So, it may be impossible to develop it without such a limitation.

Also, the process of this development and this induce are same to the application of ordinary method only. And, it is not performed by a mathematical treatment alone, but also it is performed by a thermodynamic treatment. Namely, this development is performed with the combination of the both treatments like the above description.

On the other hand, as the assembly is ideal for all components, all Q^{δ_i} is independent upon the pressure. Also, the pressure is the function of the concentration alone at the constant temperature and in the constant volume. Conseuently Q^{δ_i} is not independent upon the pressure.

Summary

The new theoretical treatment was applied to the

homogenous fluid on the basis of statistical mechanics. Also, it is considered that the homogeneous liquid is made from many particles or molecules.

In the relation between the free energy of Helmholtz, F, and the volume, according to the partial differentiation of F for the volume, the conjugated force against the volume was led.

In the case as collodial solution, the force described above was led also. And, from the determined forces for various concentrations, the molecular weight of colloidal particle and the volume occupied by the 1 mole are able to be decided.

Also, in the case that several ideal components can not pass through the semipermeable membrane, when the condition is limited, $\Pi=\overset{t}{\underset{i=0}{\Sigma}}n^{\delta_i}\dfrac{RT}{\mathbb{V}_A}$ can be obtained.

On the other hand, in the case of gas, as all component δ_i is ideal, $P\mathbb{V}=\overset{i=S}{\underset{i=0}{\Sigma}}n^{\delta_i}RT$, namely the law of ideal gas, can be obtained. Moreover, for homogenous fluid, the relation respecting the free energy of Helmholtz against the pressure or the relation respecting the free energy of Gibbs against the pressure was obtained. And, the relation is related to compressibility coefficient partially.

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Foor note — This report (Part 10) has been written out on September 25th 1986. However, the rigorous restriction was one person one contribution one year. Its restriction is available now. So, this report is received on September 20th, 1990.Morever, 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10報　均一流体に対する統計力学一部との関係

堀　津　圭　佑

　新理論的取扱を統計力学を基にし均一流体に応用した．また，均一液体は多くの粒子や分子からつくられていることを考慮した。

　Helmholty の自由エネルギー，F，と容積との関係において，容積に対するFの偏微分により，容積に対する共役力を導いた．

　コロイド溶液の場合に，上記の力をまた導いた．そして，種々の濃度に対し測定された力からコロイド粒子の分子量と1モルによって占められる容積を決定できる．

　また，いくつかの理想成分が半透膜を透過しえない場合に，その条件が制限されているとき，

$$\Pi = \sum_{i=0}^{t} n^{\delta i} \frac{RT}{V_A} \quad \text{を得ることができる．}$$

　他方，気体の場合，全成分δ_iが理想的であれば，

$$PV = \sum_{i=0}^{i=s} n^{\delta i} RT \quad \text{すなわち，理想気体の法則を得ることができる。さらに，均一流体に対}$$

し，圧力に対するHelmholtzの自由エネルギーとの関係や圧力に対するGibbsの自由エネルギーとの関係を得た。そして，その関係は圧縮係数と部分的に関係している。