

One Theoretical Treatment of Chemical Reaction

Part 9 Relation to Statistical Mechanics of Partially Homogenous Fluid

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Introduction

The concept, consideration, idea, or theoretical treatment published on the previous papers^{1~25)} was applied to the gaseous phase that was homogenous mainly. So, the concept, or other is tried to apply to the liquid phase that is homogenous as the first step. Namely, there is one common point between a homogeneous gaseous phase and a homogeneous liquid phase. It is thought that these phases are constituted of the particle. But the number, freedom of motion, or behavior of particle is different between the both phases. So, when a number of particles exist in a constant volume, it is reasonable that the freedom of motion or the behavior must be restricted with the interaction of particle. Then, the ideal state is treated at the first step. And, to make to understand the concept easily, a particle is substituted by a molecule is proposed at the next step. However, it is not always exact or precise. Only, it is one consideration under an ideal condition.

Experimental and Results, Gedanken Experiment

One propose about the definition of the homogeneous fluid is tried in the case I or II. Namely, I indicates that the homogenous fluid is the assembly. II indicates the one part of the assembly. And each assembly possesses the following properties. The only one external parameter is volume. And Q^δ of all component is constant at any position in the volume that the assembly occupies. Also, Q^δ is

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related to the temperature, the pressure, and the chemical composition only. Moreover, it is not related to the absolute magnitude of volume.

If Q^δ of one component is not related to the concentration of the component, the homogeneous fluid is called as an ideal solution respecting the component. And the component is called as an ideal component. Also, the homogeneous fluid composed with the residual component that the component is excepted is called a solvent. When the component is diluted completely, the work $-kT \log b^\delta$ respecting the component molecule δ (the molecule composes the component) of the component is constant without regard to the concentration of the dilute component. And it is expected that the homogeneous fluid becomes ideal respecting the component. Also, it goes without saying that the work $-kT \log q^\delta$ is related to Q^δ closely. Moreover, the following condition is regarded as a necessary condition. Namely, $[\sigma]$ in Q^δ is small completely, but it possesses a constant magnitude.

The homogeneous fluid that is ideal respecting all component is called as perfect gas or gas in a word.

Then, it is assumed that the following liquid is constructed with the following components and the following membrane. Namely, the semipermeable membrane that does not pass δ only divides an ideal liquid A relating to a component δ_0 from the solvent B composed with other components, $\delta_1, \dots, \delta_s$. And the following condition is assumed at the next step. Namely, the whole assembly occupies a constant volume, and the solvent exists at equilibrium each other. Also, B is large enough, and the pressure and the chemical composition are unchangeable

truly when the semipermeable membrane shifts.

Now, some relations published on the previous papers are showed for the understand of the concept as the following equations, eq. (IX-1), and eq. (IX-2).

$$p^{\delta} = \frac{Q^{\delta}}{N^{\delta}} \quad (\text{IX-1})$$

$$\mu^{\delta} = -RT \log p^{\delta} \quad (\text{IX-2})$$

Then, from the two equations, eq. (IX-1) and eq. (IX-2), the value Q^{δ} , consequently, the value of μ^{δ} is not related to the absolute magnitude of the liquid at the constant temperature. But, as the value is related to the pressure and the composition only, the free energy of Gibbs G of the homogeneous fluid is showed by the following equation, eq. (IX-3), in the relation showed as the following equation, eq. (IX-4), that was published on the previous paper.

$$G = \sum_i n_i^{\delta} \mu^{\delta i} \quad (\text{IX-3})$$

$$\mu^{\delta} = \overline{G}_p^{\delta} \quad (\text{IX-4})$$

Consequently, the free energy of Helmholtz F is showed by the following equation, eq. (IX-5), according to the relations published on the previous papers. So, moreover, these relations are showed by the following equations, eq. (IX-6) and eq. (IX-7), for an understanding.

$$F = \sum_i n_i^{\delta} \mu^{\delta i} - P \mathcal{V} \quad (\text{IX-5})$$

$$\mu^{\delta} = \sum_g \nu_g \mu^{\delta g} \quad (\text{IX-6})$$

$$G_A = F_A + P_A \mathcal{V}_A \quad (\text{IX-7})$$

Here, n_i^{δ} is the number of mole of the component δ_i . Therefore, F of the part A or F of the part B is showed as each following equation, eq. (IX-8) or eq. (IX-9), respectively.

$$F_A = n^{\delta o} \mu^{\delta o} + \sum_{i=1}^{\delta} n_A^{\delta i} \mu_A^{\delta i} - P_A \mathcal{V}_A \quad (\text{IX-8})$$

or

$$F_B = \sum_{i=1}^{\delta} n_B^{\delta i} \mu_B^{\delta i} - P_B \mathcal{V}_B \quad (\text{IX-9})$$

And, if the equilibrium in the solvents is assumed, the relation showed as the following equation, eq. (IX-10), is obtained by the following equation, eq. (IX-11), and the equation, eq. (IX-2), that was

published on the previous paper.

$$\mu_A^{\delta i} = \mu_B^{\delta i} = \mu^{\delta i} = \text{constant}, \quad i=1, \dots, S \quad (\text{IX-10})$$

$$p^{\delta A} = p^{\delta B} = \dots \quad (\text{IX-11})$$

If the sum, $n_A^{\delta i} + n_B^{\delta i}$, is represented with $n^{\delta i}$, the following relation showed as the following equation, eq. (IX-12), is obtained about F of the whole assembly.

$$F = F_A + F_B = n^{\delta o} \mu^{\delta o} + \sum_{i=1}^{\delta} n^{\delta i} \mu^{\delta i} - P_A \mathcal{V}_A - P_B \mathcal{V}_B \quad (\text{IX-12})$$

When F is partial differentiated in regard to \mathcal{V}_A , the force, $\pi^{\delta o} = P_A - P_B$, which is conjugated to \mathcal{V}_A can be obtained. Consequently, from the relation of eq. (IX-10) and the following equation, eq. (IX-13), the relation showed as the following equation, eq. (IX-14), is obtained.

$$\mathcal{V}_A + \mathcal{V}_B = \text{constant} \quad (\text{IX-13})$$

$$\begin{aligned} P_A - P_B &= - \left(\frac{\partial F}{\partial \mathcal{V}_A} \right)_T \\ &= - n^{\delta o} \left(\frac{\partial \mu^{\delta o}}{\partial \mathcal{V}_A} \right)_T + P_A - P_B + \mathcal{V}_A \left(\frac{\partial P_A}{\partial \mathcal{V}_A} \right)_T \end{aligned} \quad (\text{IX-14})$$

Namely, the following relation showed as the following equation, eq. (IX-15), is obtained.

$$\mathcal{V}_A \left(\frac{\partial P_A}{\partial \mathcal{V}_A} \right)_T = n^{\delta o} \left(\frac{\partial \mu^{\delta o}}{\partial \mathcal{V}_A} \right)_T \quad (\text{IX-15})$$

On the other hand, the following relation showed as the following equation, eq. (IX-16), is obtained from both eq. (IX-1) and eq. (IX-2).

$$\mu^{\delta} = \mu_i^{\delta} + RT \log N^{\delta} \quad (\text{IX-16})$$

Here, the following relation showed as the following equation, eq. (IX-17), is recognized.

$$\mu_i^{\delta} = -RT \log Q^{\delta} \quad (\text{IX-17})$$

Then, Q^{δ} of ideal component is a function of pressure alone at a constant temperature. And as the relation showed as the following equation, eq. (IX-18), is valid, the following relation is obtained as the following equation, eq. (IX-19).

$$N^{\delta o} = n^{\delta o} / \mathcal{V}_A \quad (\text{IX-18})$$

$$\left(\frac{\partial \mu^{\delta o}}{\partial \mathcal{V}_A} \right)_T = \left(\frac{\partial \mu_i^{\delta o}}{\partial P_A} \right)_T \left(\frac{\partial P_A}{\partial \mathcal{V}_A} \right)_T - \frac{RT}{\mathcal{V}_A} \quad (\text{IX-19})$$

Moreover, the following relation showed as the following equation, eq. (IX-21), is obtained from both eq. (IX-16) and the following equation, eq. (IX-20), that was published on the previous paper.

$$\left(\frac{\partial \mu^{\delta}}{\partial P_A}\right)_T = \overline{V}_A^{\delta} \quad (\text{IX-20})$$

$$\left(\frac{\partial \mu^{\delta_0}}{\partial P_A}\right)_T = \overline{V}^{\delta_0} = \left(\frac{\partial \mu^{\delta_0}}{\partial P_A}\right)_T + RT\beta_A \quad (\text{IX-21})$$

Here, β_A is compressibility coefficient, and can be represented by the following equation, eq. (IX-22).

$$\beta_A = -\left(\frac{\partial \log \overline{V}_A}{\partial P_A}\right)_T \quad (\text{IX-22})$$

Discussion and Conclusion

It is thought that the freedom of motion of the particle in the space is limited by the following various conditions at least; the magnitude of the space is large or small, the distribution of the particle in the space is homogeneous or heterogeneous, the interaction among the particles does not exist in the space or not, the space is held at constant or variable temperature, the pressure in the space is 1 atm or not, the space is kept at adiabatic condition or not, and others. Then, many parameters that represent the condition of the space must be established. But, the theoretical treatment of such many parameters is very complicate and much difficult. Or, the solution for such problem requires one large electronic computer that is not established or may be close to impossibility under the present investigative condition. So, in the possible range or in the reasonable restricted range, the solution for such problems was satisfied partially with the application of consideration of partial differentiation method that was used often in the thermodynamics or the physical chemistry. And, one good result was obtained with the above described method. Of course, as other calculation method that higher order determinant is used is tried under a different condition, the results may be published in future.

The particles are aggregates of many molecules, of similar molecules sometimes, of dissimilar molecules sometimes. So, it is thought that a particle is transformed to a molecule conceptually like the following case ; a particle moves independently each one without interaction. Namely, such a state is thought as one kind of ideal state. This thought is one of theoretical typical treatment. As the real state

is much complicate, the state is very difficult to treat or analyze. So, according to a means of partial differentiation, these treatments or analyses are developed step by step.

Now, this theoretical treatment is based on the behavior of particle. And its consideration is developed into the molecule from the particle. Moreover, this treatment must be developed step by step as the specificities are considered. So, the phase treated with this treatment method is homogenous as the first step. Further, the phase may be developed into a heterogenous phase that is very complicate.

About the specificity between a homogenous gaseous phase and a homogeneous liquid phase, the latter is constituted with lots of particles in a constant volume and the former is constituted with less particles than the latter. As the results, the more the particle exists, the more the motion of particle is restricted in a constant volume. If the particle is substituted with the molecule under this consideration, this concept may can be understood easily, but this shortened and convenient explanation is not precise. Exactly, there are some differences in the properties between a particle and a molecule. Therefore, there are much differences between gaseous phase and liquid phase. Then, the restrict is proposed in each case. As if a partial differentiation is applied in the thermodynamics as the above description, the one limitation, condition, or state is fixed at the first step. Next, the other limitation, the second condition, or the next state is fixed at the second step.

The motion of particle or the shift of molecule may be understood conveniently conceptually through a special net or a semipermeable membrane. However, when the liquid phase is considered, the gaseous phase, gaseous part, is coexisted with the liquid phase, liquid part. This point of coexistence induces more complicate limitations, and requires more complex considerations.

Summary

This new theoretical treatment is developed to the liquid phase. The homogenous fluid that is one

typical object of the liquid phase is defined. Moreover, the ideal solution that is composed with the ideal component is defined. And, it is treated with this theoretical treatment that the ideal component of the objective ideal fluid is divided with semipermeable membrane in the decided volume.

The free energy of Gibbs or Helmholtz of the homogenous fluid is defined.

$$G = \sum_i n_i^{\delta i} \mu^{\delta i}, \quad F = \sum_i n_i^{\delta i} \mu^{\delta i} - P\bar{V}$$

The free energy of Helmholtz of the both part *A* and part *B* that are divided with semipermeable membrane are defined.

The relation between the chemical potential and the volume or the relation between the chemical potential and the pressure is defined respectively. And a compressibility coefficient is defined.

References

- 1) L. Pauling, E. B. Wilson; Introduction to Quantum Mechanics, McGRAW-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; Statistical Thermodynamics, Cambridge Univ. Press., 1964, Cambridge
- 12) R. P. Feynman, A. R. Hibbs; Quantum Mechanics and Path Integrals, McGRAW-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. Prentice-Hall, 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.*, 26 123 1986
- 25) K. Horitsu; *ibid.*, 26 127 1986

Foot note—This report (Part 9) 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 July 15th 1988. Moreover, 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9報 均一流体に対する統計力学一部との関係

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新理論的取扱を液相に発展させた。液相の一典型的目的である均一流体を定義づけた。さらに、理想成分で組成された理想液体を定義づけた。そして、目的の理想流体の理想成分がきめられた容積内で半透膜により区分されていることをこの理論的取扱で取扱った。

均一流体の Gibbs や Helmholtz の自由エネルギーを定義づけた。

$$G = \sum_i n_i^{\delta i} \mu^{\delta i}, \quad F = \sum_i n_i^{\delta i} \mu^{\delta i} - P V$$

半透膜で区分された两部分AとBのHelmholtzの自由エネルギーを定義づけた。

化学ポテンシャルと容積との関係や化学ポテンシャルと圧力との関係につき、それぞれ定義づけた。そして、圧縮係数を定義づけた。