

One Theoretical Treatment of Chemical Reaction

Part 12 Characteristics Number of Reaction

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(Received on September 29, 1993)

Introduction

This new theoretical treatment was applied to liquid phase, homogeneous fluid and heterogeneous fluid, on the basic theory in gas phase like the previous papers.^{1~28)} Especially, the important characteristics (specific property) of reaction was tried to express with someone expression, for example, the order of reaction which was one of characteristics number on this paper.²⁹⁾ However, those following theoretical treatments are also the objective problems that are tried moreover. Namely, such a theoretical consideration is tried to apply on those various points; the concentration of chemical species, the number of molecule (particle) per unit volume, the rate of reaction per unit time or the collision rate, the hindrance or frequency of collision, and others.

Experimental and Results, Gedanken Experiment

Order of reaction:

Among the numbers that point the characteristics of reaction, the order gives the most important information about the mechanism. Each chemical species δ_i^L that constitutes the reactant in the homogeneous fluid is contained in the concentration of $N^{\delta_i^L}$, but the homogeneous fluid is part of the remarked assembly. Also, it

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is assumed that the product is not contained completely. And it is assumed that the reactant changes to the product at the rate of per unit volume of the homogeneous fluid in the homogeneous reaction, or per unit volume of the heterogeneous fluid. In this case, the order is defined as the following equation.

$$m = \sum_i \frac{\partial \log \vec{R}_o}{\partial \log N^{\delta_i^L}} \quad (\text{XII-1})$$

And $\frac{\partial \log \vec{R}_o}{\partial \log N^{\delta_i^L}}$ in each term of the right side of equation,

$$\text{namely, } m_i^L = \frac{\partial \log \vec{R}_o}{\partial \log N^{\delta_i^L}} \quad (\text{XII-2})$$

Then, it is assumed that κ , transmission coefficient, is kept in constant during the progress of reaction. And the orders of various reactions on the basis of many rate equations are considered.

At the first step, in the case of homogeneous simple reaction, according to the definition, the following equations are showed.

$$\vec{R}_o \equiv \vec{v}_1, \quad \delta^L \equiv \delta^I, \quad \delta^R \equiv \delta^F \quad (\text{XII-3})$$

$$P^{\delta^L} \equiv P^{\delta^I}, \quad P^{\delta^R} \equiv P^{\delta^F} \quad (\text{XII-4} \cdot \text{L}), (\text{XII-4} \cdot \text{R})$$

In the case of simple reaction, it may be different between $(v_i^I \text{ and } v_i^L)$, and $(v_j^F \text{ and } v_j^R)$. To this difference, the coefficient v_i^L of chemical equation may be selected to equal to the number of piece, v_i^I , of the necessary δ_i^I for

make one δ^* .

Here, \vec{v}_1 is the rate of the elementary reaction per unit volume of homogeneous fluid. If P^{δ^L} and P^{δ^R} are expressed as the following equations, (XII-5•L) and (XII-5•R) according to $P^\delta = \prod_i (P^{\delta_i})^{\nu_i}$ and $\delta^L = \sum_i \nu_i^L \delta_i^L$, $\delta^R = \sum_i \nu_i^R \delta_i^R$.

According to the equations, (XII-3), (XII-4•L), (XII-4•R) and $\vec{v}_1 = \frac{\vec{v}}{V} = \kappa \frac{kT}{h} \frac{Q^{\delta^*}}{P^{\delta^1}}$, the following equation, (XII-6) is obtained.

$$\vec{R}_0 = \kappa \frac{kT}{h} \frac{Q^{\delta^*}}{\prod_i (Q^{\delta_i^L})^{\nu_i^L}} \prod_i (N^{\delta_i^L})^{\nu_i^L} \quad (\text{XII-6})$$

Then, during the progress of reaction, all Q^{δ} is constant. In the other words, if all components that the concentration change is ideal, \vec{R}_0 is proportional to $\prod_i (N^{\delta_i^L})^{\nu_i^L}$. Consequently, the order is given from the equations (XII-1) and (XII-2) as follows;

$$m = \sum_i \nu_i^L \quad (\text{XII-7})$$

$$m_i^L = \nu_i^L \quad (\text{XII-8})$$

Namely, the order, m_i^L , related to δ_i^L is equal to the number, ν_i^L , of chemical species, δ_i^L , that reacts, the order, m , is equal to the total number of such a molecule. Conversely, if the observation value of m_i^L of the one reaction is equal to stoichiometrical coefficient, ν_i^L , of each chemical equation, the reaction may be simple reaction. Of course, the conclusion that is a simple reaction can be induced from this fact alone.

At the second step, in the case of the heterogeneous simple reaction, the following equation, (XII-9), is induced according to (XII-3), (XII-4•L), (XII-5•L), and

$$\vec{v}_1 = \frac{\vec{v}}{A} = \kappa \frac{kT}{h} G_1 \frac{Q_{\delta^*}^{\delta^*}}{P^{\delta^*}} \Theta_{\delta^*}^{\delta^*}.$$

$$\vec{R}_0 = \kappa \frac{kT}{h} G_1 \frac{Q_{\delta^*}^{\delta^*} \Theta_{\delta^*}^{\delta^*}}{\prod_i (Q^{\delta_i^L})^{\nu_i^L}} \quad (\text{XII-9})$$

If $Q^{\delta_i^L}$ and $Q_{\delta^*}^{\delta^*} \Theta_{\delta^*}^{\delta^*}$ are kept to constant during the progress of reaction, \vec{R}_0 is proportional to $\prod_i (N^{\delta_i^L})^{\nu_i^L}$ in the homogeneous fluid. Consequently, the similar conclusion to the case of homogeneous simple reaction is set up in connection with m and m_i^L .

At the next step, the homogeneous reaction that all components are composed with some elementary reactions existed in an ideal state is considered. But, the concentrations of the all components are changeable. At first, \vec{R}_0 is equal to \vec{v}_1 of the rate-determining step according to the conclusion. Namely, the rate of the rate-determining step decides the rate of the over-all reaction. Or \vec{R}_0 shows the constant ratio. Also, according

$$\text{to the equation, } \vec{v}_1 = \frac{\vec{v}}{V} = \kappa \frac{kT}{h} \frac{Q^{\delta^*}}{P^{\delta^1}},$$

this \vec{v}_1 is dependent upon only P^{δ^1} of the rate-determining step as the ideal state is assumed. And according to the conclusion that the rates of the both directions are balanced, all elementary reactions except the rate-determining step are at equilibrium. So, P^{δ^1} can be expressed as the function only P^{δ^L} according to the usage of the equation, $P^{\delta_A} = P^{\delta_B} = \dots$. Moreover, P^{δ^L} is depended upon only $N^{\delta_i^L}$. Therefore, the order, m_i^L , is given as follows;

$$\begin{aligned} m_i^L &= \frac{\partial \log \vec{R}_0}{\partial \log N^{\delta_i^L}} \\ &= \frac{\partial \log v_1}{\partial \log P^{\delta^L}} \frac{\partial \log P^{\delta^1}}{\partial \log P^{\delta^L}} \frac{\partial \log P^{\delta^L}}{\partial \log N^{\delta_i^L}} \quad (\text{XII-10}) \end{aligned}$$

However, the first term and the third term of the right side of the equation, (XII-10), are respectively equal to -1 according to the equations,

$$\vec{v}_1 = \frac{\vec{v}}{V} = \kappa \frac{kT}{h} \frac{Q^{\delta^*}}{P^{\delta^1}} \text{ and } P^{\delta^1} = \frac{Q^{\delta}}{N^{\delta}}.$$

Then, the following equation is obtained as follows;

$$m_i^L = \frac{\partial \log P^{\delta^1}}{\partial \log P^{\delta^L}} \quad (\text{XII-11})$$

The value is related to the mechanism.

Discussion and Conclusion

There are the respective important characteristics in the formless part (theory, consideration, etc.), and the form part (experiment, reaction, etc.). So, the important information of those characteristics must be shown with anyone was considered reasonably from a point of new theoretical treatment. Then, the one part is shown as follows.

As one of the expression, the order of reaction is tried to pick up. Namely, the order, m , is defined and is shown. And the order related to δ^L is also shown as the general expression, m^L .

Moreover, in the case of homogeneous simple reaction, some types are shown in the information of characteristics. Especially, the order, m^L , is equal to the number of chemical species, ν^L .

This consideration induced on this report was applied to the practical problem. Namely, the case of homogeneous para-ortho conversion reaction, $p\text{-H}_2 \rightarrow o\text{-H}_2$, of hydrogen is considered. If the elementary reaction, $\text{H} + p\text{-H} \rightarrow o\text{-H}_2 + \text{H}$, is the rate-determining step, the equilibrium relation,

$$(P^{p\text{-H}_2})^{\frac{1}{2}} = P^{\text{H}} P^{p\text{-H}}$$

is given between $\delta^L \equiv p\text{-H}_2$ and $\delta^I \equiv \text{H} + p\text{-H}$ which is the rate-determining step. Then, the relation,

$$m = m^L = \frac{3}{2}, \text{ is obtained.}$$

This value is same to the value (order) of reaction that is obtained with the experiment. Thus, the point for the mechanism can be given according to the decision of the order, m , or m^L obtained experimentally.

If the component that the concentration is changeable is at ideal state, and if $\mathcal{Q}_{\delta^*}^{\delta^*} \Theta_{\delta^*}$ is kept at constant completely, the similar conclusion in the case of the heterogeneous reaction is step up in the case of the homogeneous reaction resulting from the understand of the equation,

$$\vec{v}_1 = \frac{\vec{v}}{A} = \kappa \frac{kT}{h} G_1 \frac{\mathcal{Q}_{\delta^*}^{\delta^*}}{P^{\delta^*}} \Theta_{\delta^*}$$

In the case of the homogeneous reaction, as the concentration that the component is changeable is small,

the estimate that those components are ideal can be made often. Consequently, the important and beneficial information is given from the order about the mechanism of the reaction. Against this estimate, if a certain measure of information about the mechanism in the case of the heterogeneous reaction can not be obtained, the confirms that $\mathcal{Q}_{\delta^*}^{\delta^*} \Theta_{\delta^*}$ is kept at constant completely during the

reaction or not is almost impossible. Then, the order can not be available to clarify the mechanism. The results of experiments induce and decide the conclusion practically.

The concentrations of all components are changeable is assumed. And some elementary reactions are at the ideal state. \vec{R}_o is equal to ν_1 that is the rate-determining step. Or \vec{R}_o points a constant ratio. Under this condition, the system of reaction of the rate-determining step in the reaction passes almost into the all reactant and does not pass almost into the product. Then, the system of formation passes almost into the product and does not pass almost into the system of formation. Consequently, all of the system of reaction at the rate-determining step is formed really with the reactant, most of the system of formation passes almost into the product. Therefore, the system of reaction element reacts completely. Namely, to the condition that the state of reactant changes to the state of product, the get over the rate-determining step is necessary and sufficient.

On the other hand, the reaction is stationary (steady) state. Namely, to the intermediate products are not accumulated and are progressed, the rate difference between one direction and its reverse direction in all elementary reactions must be equal to the rate difference at the rate-determining step or must be less than it. And, as the forward and backward rates at the rate-determining step are negligible small in comparison with the rate of elementary reaction, the rate difference at the rate-determining step is negligible small in comparison with the rate of the other elementary reaction. Therefore, the rate difference at the elementary reaction except the rate-determining step is negligible small in comparison with the rates of the both directions.

Thus, the above-described two cases must be considered at least. The order of chemical reaction must be decided with the experimental results. Sometimes, the decision by estimate based on the chemical equation from the

numerical mathematical point only produces often a large mistake. This point must be called a person's attention so much to decide it.

Summary

Each reaction possesses the characteristics (specific property). The characteristics can be expressed with the characteristics number. Then, this important characteristics of reaction was tried to express with the order as one of expression form. This theoretical consideration was on the base of gas phase and its consideration was applied to liquid phase. And the first try was done to the homogeneous fluid, and the second try was done to the heterogeneous fluid.

The order, m , is expressed as follows;

$$m = \sum_i \frac{\partial \log \vec{R}_o}{\partial \log N^{\delta_i^t}}$$

So, if chemical species, δ_i^t , is related, the order, m_i^t , is expressed as follows;

$$m_i^t = \frac{\partial \log \vec{R}_o}{\partial \log N^{\delta_i^t}}$$

Moreover, the equation is developed as follows;

$$m_i^t = \frac{\partial \log \mathcal{P}^{\delta_i^t}}{\partial \log \mathcal{P}^{\delta_i^t}}$$

Then, the value is related to the expression of mechanism of reaction.

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 Mechsnics, Addison-Wesley Pub. 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 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. Penum 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. Lavenda; 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.*, 33 1 1993
- 29) K. Horitsu; *ibid.*, 34 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12報 反応の特性数

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(平成 5 年 9 月 28 日 受理)

各反応は特性（特異的性質）をもっている。その特性は特性数で表示されることができる。そこで、この反応の重要な特性が表示型の 1 つとして次数をもって表示するべく試みられた。この理論的思考は気相を基にしていたし、その思考は液相へ応用された。そして、第 1 の試みは均一流体になされ、そして第 2 の試みは不均一流体になされた。

次数, m , は次のように表示される。

$$m = \sum_i \frac{\partial \log \vec{R}_o}{\partial \log N^{\delta_i}}$$

そこで、もし化学種, δ_i^L , が関係するならば、その次数, m_i^L , は次のように表示される。

$$m_i^L = \frac{\partial \log \vec{R}_o}{\partial \log N^{\delta_i^L}}$$

さらに、その式は次のように展開される。

$$m_i^L = \frac{\partial \log P^{\delta_i^L}}{\partial \log P^{\delta_i^L}}$$

そこで、その値は反応の機構の表示と関係がある。