

One Theoretical Treatment of Chemical Reaction

Part 1 Application to Chemical Reaction in General Case

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Introduction

It is considered that general material is produced with collision and chemical bonding of molecule setting up for molecular level. This consideration, Gedanken experiment, is carried on as one of various theoretical considerations. And, if such a theoretical consideration were set up for atomic level, other theoretical consideration may be proposed.

Then, if one investigative object in chemical reaction were to set on change of component, naturally factors of equilibrium and time must be induced into the consideration and the analysis of mechanism of chemical reaction. Also, chemical equilibrium and rate of chemical reaction rise on the investigative object at the first step.

For chemical equilibrium, thermodynamics was very useful tool for analysis of chemical reaction. Then, a modern investigative method, chemical thermodynamics, was published as one means of precise treatment. The defined physicochemical quantity of each component, partial quantity, was proposed by Gibbs¹⁾ at first. And it was developed by Lewis²⁾ into a modern theoretical system of chemical thermodynamics. The induction of partial quantity facilitated an application of chemical thermodynamics. Also, the induction was reached the certainty that the modern system would be successful. So, the modern system is constituted with these partial quantities. Some publications^{3~19)} are referred to consider the concept of this theoretical treatment.

Thus, statistical mechanics is applied to chemical reaction. Moreover, the following two applications are expected; chemical statistical mechanics not only is applied to chemical equilibrium, but also is applied to rate of chemical reaction. However, these new applications are not so easy in comparison with the case of thermodynamics. Many kinds of definition are decided at the first step. So, the development of theory is performed by combining these definitions.

Experimental and Results, Gedanken Experiment

Chemical reaction: When one equilibrium system that the combination of the element among the chemical species is changed with one kind of treatment shifts to the new equilibrium system, it is said that the chemical reaction is occurred with the treatment. However, the new equilibrium system must include the different chemical species from the origin. The material system existed at the state that the property changes quickly with time is said the reacting system. At a micro-scopic physical meaning, the reacting system may be taken as a function of time.

And, according to the present chemical reaction theory, the chemical reaction is considered as the result of the whole sum of several elementary reactions that each reaction occurs independently. At a certain time, the number of elementary reaction becomes considerable large number. So, the over all reaction is considered as the sum of many elementary reactions. So, the aggregation of several combined elementary reactions under the condition that the chemical equation is satisfied is called as mechanism of chemical reaction. The satisfaction of chemical equation means

a perfect description of the experimental results adequately and exactly. Also, the satisfaction means a perfect expression of the stoichiometrical relation.

The over all chemical reaction constituted with elementary reaction is written generally as

$$\delta^L = \delta^R \quad (I-1)$$

where δ^L , or δ^R is called as the reactant, or the product respectively. Generally, the reactant is constituted with ν_Q^L pieces of chemical species δ_Q^L and the product is constituted with ν_r^R pieces of chemical species δ_r^R correspondingly. The reactant and the product are defined by

$$\delta^L = \sum_Q \nu_Q^L \delta_Q^L, \quad \delta^R = \sum_r \nu_r^R \delta_r^R \quad (I-2), (I-3)$$

When ν_Q^L and ν_r^R is selected as minimum integer in these equations, eq. (I-1) is called as chemical equation.

Also, a set of element that is related to elementary reaction is called as the reacting complex generally. Especially, the reacting complex existed at the initial state or the final state is classified from the reactant or the product of the over all reaction. So, the former or the latter is called as the initial complex or the final complex respectively.

The initial complex is constituted with ν_i^I pieces of δ_i^I . And the final complex is likewise constituted with ν_f^F pieces of δ_f^F . Namely,

$$\delta^I = \sum_i \nu_i^I \delta_i^I, \quad \delta^F = \sum_f \nu_f^F \delta_f^F \quad (I-4), (I-5)$$

Equilibrium; Thermal equilibrium: The concept is assumed as follows; in reacting system, the elementary reaction does not occur with the other elementary reaction that occurs simultaneously according to the defined and decided relation. Moreover, the elementary reaction occurs each other independently as mentioned above. This concept is one of very important assumption in modern chemical reaction theory. Moreover, another important assumption is postulated. At first, the rate of elementary reaction is only decided with the chemical composition of the assembly at that time under the conditions of the given temperature and the given external parameter, it is independent of the origin of the assembly. Namely, speaking from macro scale point of view, it becomes that it does not include a

factor of time externally. And there is the basic premise that two assumptions are approved like the above description.

On the premise, the rate of over all chemical reaction that the rate of each independent elementary reaction is summed can be calculated with the method of statistical mechanics. Also, this operation of the calculating is the object with the planning of mechanical analysis in this Gedanken experiment.

If the observed assembly is allowed to stand under the defined and decided external condition, the chemical composition changes depending upon various elementary reactions. And, its assembly reaches the equilibrium at last. Moreover, it is considered that the chemical composition fluctuates more and less with the occurrences of reactions in forward and backward directions of various elementary reactions in the assembly existed at such an equilibrium. On the other hand, it must be considered that the over all chemical reaction progresses forward or backward direction like the case of elementary reaction. Thus, its consideration is the first characteristic point. Namely, the difference between the forward reaction and the backward reaction is observed externally or as the summarized form. Moreover, it is the second characteristic point that the considerations relating to the forward reaction and the backward reaction are deduced to various independent constituted elementary reactions.

This consideration that there are two directions in the remarked reaction is one of important, typical, specific, and basic consideration of this Gedanken experiment about the over all reaction like the elementary reaction.

Now, consider such a constitution of the canonical ensemble as follows: the canonical ensemble is constituted with the same element as the assembly that is existed at equilibrium state containing the remarked reacting complex. And its ensemble is existed under the same external condition. So, it is tried to consider that the physicochemical properties of the assembly is compared with the properties of the canonical ensemble. Of course, the great majority of component of such an ensemble is constituted with the composition that is very near to the mean chemical composition. However, the following assemblies may be exceptionally. Namely, several assemblies show the

same chemical composition as the observed assembly that the so-called irreversible reaction is progressing. So, the number of such an assembly is possible to increase completely in a very large number by increasing of the number of component of an ensemble. And the following considered concepts are belonged to one kind of physicochemical assumption that is proposed in the field of physics. And the following concept is considered as one assumption.

The chance that the specific elementary reaction occurs at a certain time and the property of the elementary reaction are given by calculating the statistical mean of the region, after the region that corresponds to the same chemical composition as the chemical composition of the remarked assembly at the time is cut off from the canonical ensemble. However, it is assumed that the canonical distribution is held in this region only. The concepts related to canonical ensemble and other ensembles are published on Part 2.

When the assembly is possible to be defined as the above described assumed condition, it is said that the assembly exists at the thermal equilibrium. The part that corresponds to Zustandsumme in the above described meaning is said the Zustandsumme of the assembly. Besides, the interpretations of Zustandsumme and its related concept may be published on other paper.

Rate of elementary reaction: The occurrence of the elementary reaction is necessary to the occurrence of which one structural change or one energy change, or the both changes in reacting complex. So, the following three cases, the case that the change of energy occurs often completely, the case that the assembly exists at thermal equilibrium, and the case that the change of occurrence of elementary reaction is decided by the structural change, are the objects of the consideration in this section. The chance is defined as the reciprocal of mean time that reacting complex exists at the initial complex.

By quantum mechanics, when the difference of energy between the two electronic states in the structure that the atomic system is decided is more larger than the energy distributed by one degree of freedom of structural change, the energy of the lowest electronic state is possible to be dealt with the structural change as a

potential of atomic system. The present considered problem is limited only in such a case. Also, it is assumed that classical mechanics is possible to be applied to the motion of the center of gravity of atom.

One pertinent solution of the problem is obtained by the determination of chance of structural change on the assumption that one objective elementary reaction occurs only in the assembly, because the chance of occurrence of elementary reaction is independent on other elementary reaction that occurs at the same time as the above descriptions. And, as it is assumed that the remarked assembly exists at thermal equilibrium, the remarked assembly is constituted with the same element as the objective assembly as mentioned above, and it constitutes the canonical ensemble with a complete large number of assembly that is existed under the same external condition as the objective assembly. So, one pertinent solution is obtained by the determination of chance of structural change of component that shows same chemical composition as one objective assembly in this ensemble.

So, the structural space for the remarked assembly is fractionated to the two regions that are corresponding to the initial complex and the final complex of the remarked reacting complex. Namely, the initial and final complexes are said as the initial region and the final region correspondingly. And the chance of occurrence of structural change is given by the determination of number of the representative point that shifts from the initial region to the final region over unit time. So, the concept is an assumption that one surface is considered on the boundary of the two regions.

Then, the representative point must pass through the surface to change the structure. However, the structural change may or may not occur if the representative point passes through the surface. Because, the representative point may be sent back to the initial region before it arrives at the final region. Consequently, the number that passes through the surface gives the upper limit of number of occurrence of structural change. Therefore, if the surface were set as the number of the passed representative point decreases to minimum number, the nice upper limit of number is obtained. Such a set surface is said as critical surface.

Now, the following two expressions are assumed at

first. The degree of freedom of the assembly that the objective elementary reaction is occurring is expressed as f . And the equation of the critical surface is expressed as $q_1 = 0$ in the phase space of $2f$ dimension that is corresponding to this assembly.

The following concepts are assumed at second. The region that q_1 is positive quantity is initial region, the region that q_1 is negative quantity is final region.

Now, accepting that the following concepts are assumed, a : q_1 exists between 0 and positive quantity dq_1 . a' : q_2, \dots, q_f exist between q_2 and $q_2 + dq_2, \dots$, between q_f and $q_f + dq_f$ respectively. b : p_1 exists between negative quantity p_1 and $p_1 + dp_1$. b'' : p_2, \dots, p_f exist between p_2 and $p_2 + dp_2, \dots$, between p_f and $p_f + dp_f$ respectively. Thus, the regions of the existences of the representative points are restricted as mentioned above, a , a' , b , and b'' . And, the numbers of such representative points as defined above are given by eq. (I-8) according to

$$\delta N = \rho \delta \nu, \quad \rho = N e^{\frac{\varphi - E}{\theta}} \quad (\text{I-5}), (\text{I-6})$$

$$\begin{aligned} N &= \int \dots \int \rho dq_1 \dots dp_f \\ &= N \int \dots \int e^{\frac{\varphi - E}{\theta}} dq_1 \dots dp_f \end{aligned} \quad (\text{I-7})$$

These relations that are induced from eq. (I-5) to eq. (I-7) are simply interpreted for an understanding on this paper. So, the detailed interpretation may be published on the following paper.

About eq. (I-5), where $\delta \nu$ is region element of phase space. If $\delta \nu$ is small enough, it can be regarded as that the density ρ is homogeneous in that space. So, the number of the representative point δN in $\delta \nu$ is expressed by eq. (I-5). About eq. (I-6) and eq. (I-7), the ensemble that Gibbs proposed as another important ensemble in conservative system is canonical ensemble. It is expressed by eq. (I-6), where N is the total number of the representative point. φ and θ are the parameters of distribution that have the dimension of energy. And φ is not independent upon θ . So, the relation is expressed by eq. (I-7). And this ensemble is suitable to represent the assembly at constant temperature.

However, as the condition, the numbers of such representative points are at canonical distribution in

the case that such objective region adapts to the defined conditions, is assumed, the derivation of equation is available. The defined conditions indicate constant temperature, external parameter and chemical composition at the first step.

$$\begin{aligned} N_s &= e^{\frac{\varphi - E}{kT}} dq_1 dq_2 \dots dq_f dp_1 \dots dp_f \\ &= N_s \frac{e^{-\frac{E}{kT}} dq_1 dq_2 \dots dq_f dp_1 \dots dp_f}{\int_I e^{-\frac{E}{kT}} dq_1 \dots dq_f dp_1 \dots dp_f} \end{aligned} \quad (\text{I-8})$$

where I points the domain of integration over total region that suits to the given condition of the initial region. However, q_1 is positive quantity at this time. And N_s points the total number of the representative point that exists in the domain of integration.

Generally, energy E is possible to be expressed by eq. (I-9).

$$E = E^* + p_1^2 / 2m_1 \quad (\text{I-9})$$

where E^* is the energy of the assembly in the case that is restricted by the surface $q_1 = 0$. This assembly is regarded as a hypothetical assembly. The case is as follows; q_1 is equal to 0 usually, namely $q_1 = 0$, consequently p_1 becomes to 0, namely $p_1 = 0$. And m_1 is the reduced mass of degree of freedom of the first, p_1/m_1 is general velocity in the direction of q_1 . Therefore, eq. (I-8) points the number of the representative point that passes through the surface $q_1 = 0$ from the side of initial region to the opposite side over the time of $(dq_1/p_1) \cdot m_1$.

Therefore, the number per unit time of the representative point that passes through the surface $q_1 = 0$ from the side of the initial region is given by dividing the eq. (I-8) by $(dq_1/p_1) \cdot m_1$. Namely, the number is expressed by eq. (I-10).

$$N_s \frac{e^{-\frac{E}{kT}} \frac{p_1}{m_1} dq_2 \dots dq_f dp_1 \dots dp_f}{\int_I e^{-\frac{E}{kT}} dq_1 \dots dq_f dp_1 \dots dp_f} \quad (\text{I-10})$$

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The total number N'_s of the representative point that passes through the surface per unit time from the side of the initial region is given by integrating eq. (I-10) for the total region of negative value of p_1 , by integrating p_2, \dots, p_f for the each total region of positive value or negative value respectively, and by integrating q_1, \dots, q_f for the total region decided with the remarked condition. Now, if this domain of integration is expressed by S' , N'_s is given from eq. (I-9), namely

$$\begin{aligned}
 N'_s &= N_s \frac{\int_{S'} e^{-\frac{E^* + p_1^2/2m_1}{kT}} \frac{p_1}{m_1} dq_2 \cdots dq_f dp_1 \cdots dp_f}{\int_I e^{-\frac{E}{kT}} dq_1 \cdots dq_f dp_1 \cdots dp_f} \\
 &= N_s \frac{\int_{-\infty}^0 e^{-\frac{p_1^2}{2m_1 kT}} \frac{p_1}{m_1} dp_1 \int_S e^{-\frac{E^*}{kT}} dq_2 \cdots dq_f dp_2 \cdots dp_f}{\int_I e^{-\frac{E}{kT}} dq_1 \cdots dq_f dp_1 \cdots dp_f} \\
 &= N_s kT \frac{\int_S e^{-\frac{E^*}{kT}} dq_2 \cdots dq_f dp_2 \cdots dp_f}{\int_I e^{-\frac{E}{kT}} dq_1 \cdots dq_f dp_1 \cdots dp_f} \quad (\text{I-11})
 \end{aligned}$$

where $\int_0^\infty e^{-ax^2} x dx = \frac{1}{2a}$ is employed for understand.

The chance that the representative point passes through the critical surface S is given by the N'_s/N_s . Now, if the ratio of the number of the representative point that completes the elementary reaction to the number of the representative point that passes through the surface S from the side of initial region is expressed with κ , the chance of the elementary reaction N'_1/N_1 is given by eq. (I-12).

$$\frac{N'_1}{N_1} = \kappa \frac{N'_s}{N_s} = \kappa kT \frac{\int_S e^{-\frac{E^*}{kT}} dq_2 \cdots dq_f dp_2 \cdots dp_f}{\int_I e^{-\frac{E}{kT}} dq_1 \cdots dq_f dp_1 \cdots dp_f} \quad (\text{I-12})$$

where κ is more than 1 or is equal to 1, namely, $\kappa \leq 1$.

The reaction that κ is equal to 1, namely, $\kappa = 1$, is called as effusion type reaction, and the reaction that κ is more and more less than 1, namely, $\kappa \ll 1$, is called as diffusion type reaction.

Then, the chance of occurrence of the elementary reaction is possible to be expressed by using of Zustandsomme of the assembly that adds the critical complex and the initial complex. So, these problems may be published on other paper.

Steady (stationary) reaction and rate determining step reaction: The reaction that is most simple in reaction mechanism is constituted with only one elementary reaction. Such a reaction is called simple reaction. However, the description of reaction mechanism necessitates several continual elementary reactions, but also many branched elementary reactions generally. When a reactant shifts a product, it is possible that the reaction passes through several different reaction processes, reaction pathways, in order to the existence of the above described various elementary reactions. Then, steady reaction, stationary reaction, that has the progressional rate determining step at thermal equilibrium is alone considered as the present problem. Here, the concept is proposed for develop this theory. Steady reaction is defined by the condition that the reaction progresses without accumulation of all intermediate product. Naturally, there is no feedback reaction. On the view point of biochemical reaction, normal growing living matter has various continual elementary reactions and many branched elementary reactions, and has an irreversible over all forward reaction in conclusion. In such biological elementary reaction ensemble, the condition of harmonization is very important factor. If the condition of harmonization does not hold for a short time, the living matter falls to the abnormal biological reaction pathways. Moreover, if the living matter can not get back the normal biological reaction pathway, it becomes that the living matter loses the life in the result.

And the concept is proposed as above described. Rate determining step is defined as the reaction that is necessary absolutely to progressing of reaction. And moreover, rate determining step is one special reaction that the rates of forward and backward reactions are as

negligibly small as possible in comparison with the rate of other any constituted elementary reaction.

When the concepts of definitions about the steady reaction and the rate determining step are assumed as mentioned above, the following concepts are concluded.

- (1) The initial complex of rate determining step of reaction shifts upon substantially all the reactant and shifts scarcely upon the product. So, the final complex shifts upon substantially all the product and shifts scarcely upon the initial complex. Consequently, it becomes that the initial complex of rate determining step is all really constituted with the reactant. Also, it becomes that the final complex shifts upon almost substantially the product. Therefore, the phenomenon that the reacting complex completes the reaction is equal to the phenomenon shifted from the state of the reactant to the state of the product. For the completion of the phenomenon, the passing over the rate determining step is necessary and sufficient condition. In other words, the rate of over all reaction is decided by the rate of rate determining step.
- (2) The phenomenon that the reaction is steady is replaced as following; namely, the intermediate product shifts without accumulation. In any elementary reaction, the difference between the rate of reaction in the one direction of reaction and the rate of reaction in the opposite direction of reaction has to be equal to or be less than it for the completion of the phenomenon.

For comprehensive understanding of the concept as mentioned above, the following simple reaction mechanism is considered as one example.



where V is the rate of reaction in each direction of the reaction respectively. Symbol' is expressed the opposite direction against nonsymbol.

And it is assumed that this reaction is steady. Namely, in the case that the intermediate product does not accumulate,

$$dB/dt = V_a - V_a' - (V_b - V_b') = 0 \quad (\text{I-14})$$

eq. (I-14) is valid. Consequently,

$$V_a - V_a' = V_b - V_b' \quad (\text{I-15})$$

eq. (I-15) is valid. From the similar reasoning to that described above, if the reaction process is not branched, it is concluded that the difference of the rate of each elementary reaction is equal to each other. However, if the reaction process, the reaction pathway, is branched, it may become that the difference of the rate of the one elementary reaction is less than the difference of the rate of the rate determining step. And, because the both rates themselves of forward and backward directions of rate determining step are negligibly small in comparison with the rate of other any elementary reaction, the difference of the rate of the determining step is naturally negligibly small in comparison with the rate of other elementary reaction. Consequently, the difference of the rate is negligibly small in comparison with the rates of the both directions in any elementary reaction except the rate determining step. In other words, it is concluded that the rates of the both directions of the reaction are at a balanced state.

Discussion and Conclusion

The duplication of contents shown in the section of Experimental and Result, Gedanken experiment, is avoided except important parts from the space of this paper.

One new theoretical treatment that the fundamental concept was on the basis of statistical mechanics, quantum mechanics, and thermodynamics was applied to many basic parts of chemical reaction in general case. This try of new theoretical treatment is one kind of experiment, Gedanken experiment, thought experiment, as such a so-called usual experiment that is not a thought experiment.

There are many objective problems to investigate chemical reaction that occurs in the fields of living matter and of non-living matter.

The basic analysis of these chemical reactions that includes the biological reaction is very important to solve the phenomena of life cycles of living matters. Of course, life cycles are depended upon the circumstances that includes various chemical reactions. Moreover, living matter can not separate from non-living matter.

One Theoretical Treatment of Chemical Reaction

The attempt of application of such a statistical mechanical treatment to one part of biological reaction is testing by the author as a new consideration for living matter. However, this region related it is very wide and this contents related it is very complicate. But, the range that is possible to investigate depends upon progressing of scientific background, but the range is becoming small year after year by the progressing.

This scientific considerations that many kinds of chemical reaction in non-living world are observed in universal, global, regional, local, polymolecular, molecular, atomic, and elementary particular fields may be applied to the complicate, holy, prior-experiential reaction in living world on a common boundary. At least, as this common boundary can be found at molecular level, the chemical reaction at molecular level is value to investigate more and more. Consequently, some fundamental parts of chemical reaction that occurred at state of molecule became one target of this consideration. Therefore, this theoretical treatment was tried for molecular reaction as shown on this paper. On the other hand, this fundamental investigation is necessary to solute many problems of biological complicate reaction.

Chemical reaction: Chemical reaction is constituted with elementary reaction. Chemical reaction that is so called usually is to be called as over all reaction. From the concept that over all reaction has forward and backward directions, the property of elementary reaction is deduced like over all reaction. Namely, elementary reaction also has forward and backward directions. Therefore, over all reaction is an aggregation of elementary reaction. Such a reaction is constituted with chemical species. And, the combination of reaction, the direction of reaction, and the chemical species are considered with reaction velocity.

Equilibrium; Thermal equilibrium: It is assumed that usually the reaction reaches equilibrium at last. From this concept, it is deduced that various kinds of parameter, ensemble, assembly are related to equilibrium closely.

It is pointed that there are four kinds, temperature, volume, pressure, and time, in equilibrium at least. In this clause of equilibrium, thermal equilibrium is only shown as a main target. And the theoretical treatment is

deduced from statistical mechanics.

Rate of elementary reaction: When over all reaction or elementary reaction occurs, it is necessary that energy goes in or goes out. Namely, energy change appears in various types with various external or internal circumstances. This problem is related to statistical mechanics, quantum mechanics, and thermodynamics. Also, here, the degree of freedom is attended to elementary reaction. Moreover, the number of molecule related to reaction and the behavior, passing through a surface, of molecule per unit time are taken up as a basic factor that is correlated with reaction velocity.

Steady reaction, stationary reaction: When all intermediate product can not be observed in progress of reaction, it is said that the reaction is steady reaction. Also, it is said that this steady reaction is reaction existed at steady state. On the other expression, a glass tube that includes running water fully is a good example of it.

Rate determining step reaction: One interpretation is tried to understand this term. Over all reaction is constituted with elementary reaction. These reactions have forward direction and backward direction, one direction and opposite direction, of each reaction. It is possible to consider that the rate determining step reaction is included in over all reaction as one elementary reaction among other elementary reactions. Moreover, it can be considered that the elementary reaction effects on sufficiently and regulates in detail the rate of over all reaction. Therefore, the rate of reaction is shown by sum of forward reaction and backward reaction. So, the rate of over all reaction is shown by sum of all elementary reactions.

Also, it is said by other expression that rate determining step fills the role of regulation of reaction. Therefore, it is understood that there is certainly rate determining step in whole reaction from one constitutional viewpoint. For example, it is an excursion of one group of different walking speed walker.

This consideration that the reaction in the field of non-living matter is set up the reaction in the field of living matter may be reasonable or natural when the progressive clarification of the biological replication of DNA or the structural and functional change of the gene by various kinds of biotechnology is thought.

The investigation of the behavior of molecule may be applied effectively in such a form.

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Summary

One new theoretical treatment that was on the basis of statistical mechanics, quantum mechanics, and thermodynamics was tried to apply to various parts of chemical reaction as Gedanken experiment.

The other basic theoretical considered results may be reported gradually on other papers.

The basic point of this consideration is a collision of molecule, a binding of molecule, and a combination of molecule with a factor of time or without a factor of time.

The above mentioned consideration was applied to the following objective problems; (1) Chemical reaction – General case, (2) Equilibrium – Thermal equilibrium, (3) Rate of elementary reaction, (4) Steady reaction and rate determining step.

This consideration or investigation about the behavior of molecule may be applied effectively in biotechnological and molecular biological fields.

化学反応の理論的取扱

第1報 化学反応一般

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(昭和57年9月27日受理)

統計力学, 量子力学, 熱力学を基にした一つの新しい理論的取扱を思考実験として種々の化学反応に試みた。他の理論的考察結果は漸次他報で報告する。

この考察の基本点は時間要素を含むか含まぬ分子の衝突, 結合, 組合せである。

上記の考察は次の目的問題へ応用された。(1)化学反応一般, (2)平衡-熱平衡, (3)素反応の速度, (4)定常反応と律速段階。

分子の行動についてのこの考察や研究は生物工学や分子生物学の分野に有効に応用されるであろう。