

On Chemical Resistance. II.

Some Applications of the Theory of Quanta to Chemical Dynamics.

By

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Three years ago, the definition, the method of calculation, and the signification of chemical resistance were described by the author in his paper "On chemical Resistance."¹ At that time, however, it was considered to be impossible to calculate chemical resistance in a direct way. During these three years, many reports of investigation into chemical kinetics have been made by several scientists and among those reports, the studies on catalysis by W. C. McC. Lewis² have no doubt had a stimulative effect upon the development of chemical kinetics. Studies in chemical statics have gradually developed on the sound foundation of thermodynamics, but as to chemical kinetics, there was no general theory based upon any exact theoretical grounds. Lewis's essays which are based upon the theory of quanta have thrown a light whereby one may evolve a fundamental theory of chemical kinetics. The above mentioned essays stimulated the author into reconsidering the direct calculation of chemical resistance. Now, that calculation of chemical resistance, a new method of deriving chemical affinity constant, and some applications of the theory of quanta on chemical kinetics will be discussed in this paper.

Chemical Resistance and its Signification.

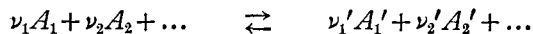
As the author has already remarked in the former paper, chemical resistance, a term first introduced by Nernst, is after the definition such as :

$$\text{Chemical Resistance} = \frac{\text{Chemical Force}}{\text{Velocity}} .$$

¹ These Memoirs I, 277, (1915).

² J. Chem. Soc., 105, 2330, (1914); 109, 796, (1916); 111, 457, 1086, (1917).

In that paper, the author has got the mathematical expression of chemical resistance according to this definition of Nernst. As an expression of reaction, we will use the following :



When the reaction occurs in a dilute solution, or in the case $\Sigma \nu = 0$, where the negative sign is assigned to ν' , the chemical resistance will be expressed as follows :

$$\mathfrak{R} = \frac{\frac{dA}{dt}}{\frac{dx}{dt}} = \frac{RT\bar{N} \{ \Sigma \ln(C_1 - \nu_1 x)^\nu - \Sigma \ln c_1^\nu \}}{k_1(C_1 - \nu_1 x)^\nu \dots - k_2(C_1' - \nu_1' x)^{-\nu_1' \dots}}, \quad (1)$$

where C_1, \dots, C_1', \dots and c_1, \dots, c_1', \dots are the initial and final concentrations of the reacting substances A_1, \dots and A'_1, \dots respectively and k_1, k_2 are the reaction constants and \bar{N} is the total number of mols in the reacting system. In the former paper, the most general case of reaction was discussed, but in the present, the reaction specified as above will be treated for the sake of simplicity of calculation.

In the first paper, the author has described the signification of chemical resistance taking the special case, $2H_2 + O_2 = 2H_2O$, as follows:

“ It consists of two terms of different properties, viz.

1. The resistance to the dissociation of the molecules, H_2 and O_2 to the atom.
2. The probability that H and O approach each other within the atomic distance by their kinetic energies.

With our present knowledge of atoms and molecules, it is impossible to calculate the chemical resistance in a direct way.”

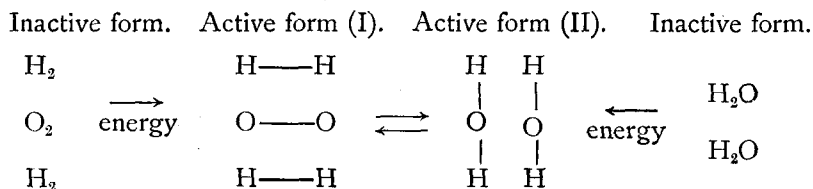
If we get the mathematical expression of resistances relating to the above two terms, we can easily get the expression of chemical resistance in a direct way. Now, in this paper, the direct calculation will be essayed according to a hypothesis about the mechanism of chemical reaction and applying the theory of quanta as Lewis has developed it.

The Two Factors of Chemical Resistance and Chemical Progressibility.

Of the mechanism of a chemical reaction, the author proposes the following hypothesis:—*The reacting substances can only react when they*

assemble together in a certain elemental sphere (*Elementargebiet*) of a reaction in a stoichiometrical relation by their own kinetic energy, but the reaction will begin only when they are transformed into the active form by absorbing some energy from the surrounding medium.

Again we will take the example: $2H_2 + O_2 = 2H_2O$. The molecules of hydrogen, oxygen, and water in this system will be constant and vigorous motion in their kinetic energies as usual with a gaseous system, but the reaction will only proceed when the two molecules of hydrogen and one molecule of oxygen or two molecules of water encounter in an elemental sphere, and moreover, these molecules become active by absorbing some energy from their surrounding medium. such as:



where we assume that there is no energy transport accompanying the mutual transformation of the two active forms (I) and (II).

According to the above hypothesis of the mechanism of a chemical reaction, chemical resistance can easily be separated into two terms.

1. A term inversely proportional to the probability that the molecules of the reacting substances encounter in a stoichiometrical relation in an elemental sphere by their own kinetic energy.

2. A term proportional to the probability of the energy transport to reacting molecules from their surrounding medium.

On this assumption, the reaction can proceed only, when the above two conditions are satisfied, then the chemical resistance can be expressed by the product of the above two terms as in the case of the probability that two independent matters occur at the same time.

For the simplicity of the calculation, we take the reciprocal of chemical resistance, say, chemical progressibility.

$$\mathfrak{R} = \frac{1}{A}$$

It is obvious that chemical progressibility is also the product of the reciprocals of the above two factors. Now, we will derive the mathematical expression for each of the above factors separately.

I. Of the reaction: $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$, the numbers of the molecules and the concentrations of the reacting substances are denoted by n_{H_2} , n_{O_2} , $n_{\text{H}_2\text{O}}$, and C_{H_2} , C_{O_2} , $C_{\text{H}_2\text{O}}$ and the total volume of this system by V . If the elemental sphere of hydrogen in this system be ϵ_{H_2} , then the number of elemental sphere of hydrogen in this system may be expressed by $\frac{V}{\epsilon_{\text{H}_2}}$, but only n_{H_2} spheres of them contain a hydrogen molecule. As to oxygen, exactly like hydrogen, the number of elemental spheres of oxygen in this system will be $\frac{V}{\epsilon_{\text{O}_2}}$, and only n_{O_2} spheres of them contain an oxygen molecule. Then the probability that two molecules of hydrogen and one molecule of oxygen meet together in an elemental sphere of reaction will be proportional to the following expression:

$$\frac{\frac{n_{\text{H}_2}}{V}}{\epsilon_{\text{H}_2}} \cdot \frac{\frac{n_{\text{H}_2}}{V}}{\epsilon_{\text{H}_2}} \cdot \frac{\frac{n_{\text{O}_2}}{V}}{\epsilon_{\text{O}_2}} = \epsilon_{\text{H}_2}^2 \epsilon_{\text{O}_2} N^3 C_{\text{H}_2}^2 C_{\text{O}_2}, \quad (3)$$

where N denotes Avogadro's constant.

II. To become reactive, a molecule must absorb some energy from its surrounding medium and according to Lewis this energy increment is equal to $h\nu$, where ν is the characteristic frequency of the molecule. But the author treats this energy increment as equal to some multiple of $h\nu$, viz., $n h\nu$, instead of $h\nu$. Let the inner energy, corresponding with the frequency ν , of one mol of the inactive and active molecules be U and U' respectively, then

$$U'_\nu = U_\nu + nN h\nu. \quad (4)$$

According to the theory of quanta,

$$U_\nu = N \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}, \quad (5)$$

or
$$\frac{h\nu}{kT} = \ln \left(1 + \frac{N h\nu}{U_\nu} \right).$$

If $\frac{h\nu}{kT} - 1 < 1$, and U_ν is quite larger than $N h\nu$, we can put

$$\frac{n h\nu}{kT} = \ln \left(1 + \frac{N h\nu}{U} \right)^n \doteq \ln \left(1 + \frac{n N h\nu}{U_\nu} \right).$$

Using the relation (4), $\frac{n h\nu}{kT} = \ln \left(1 + \frac{U'_\nu - U_\nu}{U_\nu} \right) = \ln \frac{U'_\nu}{U_\nu},$

therefore
$$nN\nu v = RT \ln \frac{U'_v}{U_v}. \quad (6)$$

When ν is quite large, we can not use the above approximation, then

$$nN\nu v = RT \ln \left(1 + \frac{U'_v - U_v}{nU_v} \right)^n = RT \ln u, \quad (6_1)$$

where u is a constant at a constant temperature.

The total energy of molecule depends upon its concentration.¹ If the total energy of one mol of inactive and active molecules be E and E' and their concentrations be C and C' respectively, then

$$\begin{aligned} E' - E = \varphi &= RT \ln \frac{C'}{C} + U' - U \\ &= RT \ln \frac{C'}{C} + nN\nu v. \end{aligned}$$

If we take the relation (6₁), $\varphi = RT \ln \frac{C'u}{C}. \quad (7)$

where φ is the energy which is needed to change one mol of inactive molecules into the active form, and to which the chemical resistance would be proportional. Supposing that this energy increment comes from the special radiant energy in the reacting medium, as Lewis has stated, the facility of the energy transport would depend on the radiant energy or the probability that the energy transport will be proportional to the radiant density. In that case the chemical resistance will be inversely proportional to the radiant density, thus

$$\mathfrak{R} \propto \frac{\varphi}{\bar{D}},$$

where \bar{D} denotes the density of the special radiant energy.

The Total Chemical Progressibility and the Total Chemical Resistance.

First of all, the resistance to the change when two mols of hydrogen and one mol of oxygen are converted into two mols of water, will be calculated. To convert one mol of hydrogen into the active

¹ The total energy of the gas may be divided into internal and external. The former consists of the kinetic energy of molecular motion and the potential energy of intermolecular forces. The external energy is measured by the work which could be performed by the gas in expanding to a state of infinite rarity starting its present configuration. (see, Jeans: the Dynamical Theory of Gases. p. 189.)

form, the following amount of energy will be needed as already described.

$$\varphi_{H_2} = RT \ln \frac{C_{H_2}' u_{H_2}}{C_{H_2}}.$$

Similarly for a mol of oxygen.

$$\varphi_{O_2} = RT \ln \frac{C_{O_2}' u_{O_2}}{C_{O_2}},$$

and similarly for a mol of water,

$$\varphi_{H_2O} = RT \ln \frac{C_{H_2O}' u_{H_2O}}{C_{H_2O}}.$$

In the mutual transformation of the active forms (I) and (II), there is no energy transport, therefore the total energy needed in the reaction $2H_2 + O_2 \rightarrow 2H_2O$, is

$$\varphi_{\rightarrow} = RT \left\{ \ln \left(\frac{C_{H_2}' u_{H_2}}{C_{H_2}} \right)^2 + \ln \frac{C_{O_2}' u_{O_2}}{C_{O_2}} - \ln \left(\frac{C_{H_2O}' u_{H_2O}}{C_{H_2O}} \right)^2 \right\}. \quad (8)$$

The two active forms must always be in equilibrium during the reaction, therefore

$$\frac{C_{H_2O}'^2}{C_{H_2}'^2 C_{O_2}'} = x,$$

then

$$\varphi_{\rightarrow} = RT \left\{ \ln \frac{C_{H_2O}'^2}{C_{H_2}'^2 C_{O_2}'} - \ln x - \ln \frac{u_{H_2O}'^2}{u_{H_2}'^2 u_{O_2}'} \right\},$$

where all of x , u_{H_2} , u_{O_2} , u_{H_2O} , are constant at a constant temperature, then

$$\varphi_{\rightarrow} = RT \left\{ \ln \frac{C_{H_2O}'^2}{C_{H_2}'^2 C_{O_2}'} - \ln K \right\}. \quad (9)$$

This energy would be obtained from the surrounding medium in the form of radiant energy of different wave lengths. If the energies $n_{H_2}'/h\nu_{H_2}$ and $n_{O_2}'/h\nu_{O_2}$ be those to actify the molecules of hydrogen and of oxygen respectively, and \bar{D}_{H_2} and \bar{D}_{O_2} be the radiant densities of those radiations in the system, then the chemical resistance of the transformation, $2H_2 + O_2 \rightarrow 2H_2O$, would be inversely proportional to the product, $\bar{D}_{H_2}^2 \cdot \bar{D}_{O_2}$, then

$$\mathfrak{R} \propto \frac{RT \left(\ln \frac{C_{H_2O}^2}{C_{H_2}^2 C_{O_2}} - \ln K \right)}{\bar{D}_{H_2}^2 \cdot \bar{D}_{O_2}}$$

But the energy $n'h\nu$ is not equal to the energy increment of the active molecule $n'h\nu$, or n' is not usually equal to n . The relation n' to n will be discussed in a later section.

Again the probability that two molecules of hydrogen and one molecule of oxygen will come into an elemental sphere of reaction, is as already described in (3), and the total chemical resistance of the transformation, $2H_2 + O_2 \rightarrow 2H_2O$, is

$$\mathfrak{R} = \frac{RT \left(\ln \frac{C_{H_2O}^2}{C_{H_2}^2 C_{O_2}} - \ln K \right)}{PN^2 \bar{D}_{H_2}^2 \bar{D}_{O_2} \varepsilon_{H_2}^2 \varepsilon_{O_2} C_{H_2}^2 C_{O_2}},$$

where P is a proportional factor,

Similarly, the total resistance of reverse reaction is

$$\mathfrak{R} = \frac{RT \left(\ln K - \ln \frac{C_{H_2O}^2}{C_{H_2}^2 C_{O_2}} \right)}{PN^2 \bar{D}_{H_2O}^2 \varepsilon_{H_2}^2 \varepsilon_{O_2} C_{H_2}^2 C_{O_2}}$$

The progressibilities of these single reactions are the reciprocals of the above expressions and the expression of the progressibility of the whole reaction: $2H_2 + O_2 = 2H_2O$, is

$$\Sigma A = \frac{PN^3 \bar{D}_{H_2}^2 \bar{D}_{O_2} \varepsilon_{H_2}^2 \varepsilon_{O_2} C_{H_2}^2 C_{O_2} - PN^2 \bar{D}_{H_2O}^2 \varepsilon_{H_2}^2 \varepsilon_{O_2} C_{H_2}^2 C_{O_2}}{RT \left(\ln \frac{C_{H_2O}^2}{C_{H_2}^2 C_{O_2}} - \ln K \right)}$$

Then the total resistance of this reaction is

$$\Sigma \mathfrak{R} = \frac{RT \left(\ln \frac{C_{H_2O}^2}{C_{H_2}^2 C_{O_2}} - \ln K \right)}{PN^3 \bar{D}_{H_2}^2 \bar{D}_{O_2} \varepsilon_{H_2}^2 \varepsilon_{O_2} C_{H_2}^2 C_{O_2} - PN^2 \bar{D}_{H_2O}^2 \varepsilon_{H_2}^2 \varepsilon_{O_2} C_{H_2}^2 C_{O_2}} \quad (10)$$

In this expression, since both $PN^3 \bar{D}_{H_2}^2 \bar{D}_{O_2} \varepsilon_{H_2}^2 \varepsilon_{O_2}$ and $PN^2 \bar{D}_{H_2O}^2 \varepsilon_{H_2}^2 \varepsilon_{O_2}$ are constants, make them equal to k_1/e_1 and k_2/e_2 respectively, where e_1 and e_2 are mol equivalent in the single reactions. In our example,

$2H_2 + O_2 = 2HO$, $e_1 = 3$, and $e_2 = 2$, but in a special case where the reaction occurs in a dilute solution, or the molecular coefficients of both sides in the reaction scheme are equal, $e_1 = e_2$, then

$$\mathfrak{R} = \frac{eRT \left(\ln \frac{C_{H_2O}^2}{C_{H_2}^2 C_{O_2}^2} - \ln K \right)}{k_1 C_{H_2}^2 C_{O_2} - k_2 C_{H_2O}^2} \quad (101)$$

Now we can get the expression of the chemical resistance of the reaction when the expression (101) is multiplied by \bar{N}/e , where \bar{N} is the number of mols in the reacting system. And it is easily seen that the expression exactly coincides with the expression (2) which was derived from Nerns't definition and this coincidence supports the hypothesis of the mechanism of a chemical reaction which was adopted here in the calculation of chemical resistance.

The Heat Toning of a Reaction.

In the mutual transport of the two active forms as stated as above, there is no energy transport. Let U_{H_2} , U_{O_2} , U_{H_2O} be the internal energies of one mol of H_2 , O_2 and H_2O at T respectively, then the heat toning Q_T of the reaction, $2H_2 + O_2 = 2H_2O$, will be equal to the sum

$$2U_{H_2} + U_{O_2} - 2U_{H_2O}. \quad (11)$$

The internal energy of one molar group of the first active form, $\begin{array}{c} \text{H-H} \\ \text{O-O} \\ \text{H-H} \end{array}$, is

$$2U_{H_2} + 2n_{H_2}N h\nu_{H_2} + U_{O_2} + n_{O_2}N h\nu_{O_2}.$$

That of the second active form, $\begin{array}{c} \text{H H} \\ | | \\ \text{O O} \\ | | \\ \text{H H} \end{array}$, is

$$2U_{H_2O} + 2n_{H_2O}N h\nu_{H_2O}.$$

These internal energies of the two active forms must be equal to each other according to the hypothesis, that is

$$2U_{H_2} + U_{O_2} - 2U_{H_2O} = -2n_{H_2}N h\nu_{H_2} - n_{O_2}N h\nu_{O_2} + 2n_{H_2O}N h\nu_{H_2O}$$

or

$$Q_T = -\Sigma nN h\nu.$$

A special case of the last expression was at first found by F. Haber¹, and recently explained by Lewis, but they did not discuss the temperature variation of Q , because they had not taken the factor n , the number of the energy quanta, into consideration. Since the temperature variation of the expression will depend only on the factor n , Nh remaining constant, we have

$$\frac{dQ_T}{dT} = -\Sigma N h \nu \frac{dn}{dT}$$

or

$$2C_{H_2,m}^{0,T} + C_{O_2,m}^{0,T} - 2C_{H_2O,m}^{0,T} = -2N h \nu_{H_2} \frac{d(n_{H_2} - n_{H_2}^0)}{dT} - N h \nu_{O_2} \frac{d(n_{O_2} - n_{O_2}^0)}{dT} + 2N h \nu_{H_2O} \frac{d(n_{H_2O} - n_{H_2O}^0)}{dT}, \quad (12)$$

where $C_{H_2,m}^{0,T}$, $C_{H_2O,m}^{0,T}$ and $C_{O_2,m}^{0,T}$ are mean molecular heats of H_2 , O_2 and H_2O respectively.

If
$$n = n_0 + n_1 + n_2 + n_3 + \dots + n_T$$

where n_1, n_2, \dots, n_T are the numbers of the energy quanta which must be added at the respective temperature $1^\circ, 2^\circ, \dots, T^\circ$, then from (12) it is clear that the real energy increments at respective temperatures are

$$n_1 h \nu, n_2 h \nu, \dots, n_T h \nu. \quad (13)$$

Moreover, it is obvious that

$$Q_0 = -\Sigma n_0 N h \nu,$$

where Q_0 is the heat tony at absolute zero degree.

A New Method of Deriving the Expression of Affinity Constant.

On a reversible chemical reaction, we have the expression for the two reaction constants such as:

$$k_1 = P^3 N^3 \bar{D}_{H_2}^2 \bar{D}_{O_2} \bar{D}_{H_2O} \epsilon_{H_2}^2 \epsilon_{O_2},$$

$$k_2 = P N^2 \bar{D}_{H_2O}^2 \epsilon_{H_2O}^2,$$

then the affinity constant K is

¹ Ber. D. physik. Ges., 13, 117, (1911).

$$K = \frac{k_1}{k_2} = \frac{\bar{D}_{\text{H}_2}^2 \bar{D}_{\text{O}_2} (N\epsilon_{\text{H}_2})^2 (N\epsilon_{\text{O}_2})}{D_{\text{H}_2\text{O}}^2 (N\epsilon_{\text{H}_2\text{O}})^2}. \quad (14)$$

Thus, if we had expressions for \bar{D} and ϵ , the affinity constant K could be calculated and it must be the same as that derived from Nernst's heat theorem.

D , the radiant density of the radiant energy $h\nu$ in the system, according to Planck's theory, is

$$D = \frac{8\pi h\nu^3 n^3}{c^3} \frac{1}{e^{\frac{h\nu}{kT}} - 1}, \quad (15)$$

where n is the index of refraction of the system with respect to ν and c is the velocity of light in vacuum. The radiation, which takes place in a chemical reaction, is commonly in the short infra-red region, and the value ν is quite large, then we put

$$e^{\frac{h\nu}{kT}} - 1 \doteq e^{\frac{h\nu}{kT}}$$

and we have

$$D = \frac{8\pi h\nu^3 n^3}{c^3} e^{-\frac{h\nu}{kT}}.$$

The energy quantum, $n'h\nu$, which must be brought to actify a molecule of hydrogen, is not equal to its energy increment $nh\nu$ when actified.

If energy increment be

$$\begin{array}{ll} n_0 h\nu & \text{at } T = 0^\circ \\ (n_0 + n_1) h\nu & \text{at } T = 1^\circ \\ (n_0 + n_1 + n_2) h\nu & \text{at } T = 2^\circ \\ \dots\dots\dots & \dots\dots\dots \\ (n_0 + n_1 + n_2 \dots\dots n_T) h\nu & \text{at } T = T^\circ \end{array}$$

The energy quantum $n'h\nu$, which must be brought to actify a molecule would be

$$\begin{array}{ll} n'h\nu = n_0 h\nu & \text{at } T = 0^\circ \\ ,, = n_0 h\nu + T_1 \frac{n_1}{T_1} h\nu & \text{at } T = 1^\circ \\ ,, = n_0 h\nu + T_2 \left(\frac{n_1}{T_1} + \frac{n_2}{T_2} \right) h\nu & \text{at } T = 2^\circ \\ \dots\dots\dots & \dots\dots\dots \end{array}$$

$$n'h\nu = n_1\nu + T\left(\frac{n_1}{T_1} + \frac{n_2}{T_2} + \dots + \frac{n_T}{T}\right)\nu \quad \text{at } T = T^\circ$$

In the above expressions, the assumption $n' = n$ at $T = 0^\circ$, is what corresponds to that of Nernst's theorem, that the entropy of a condensed system at absolute zero point is zero or $\lim_{T \rightarrow 0} \frac{dA}{dT} = \lim_{T \rightarrow 0} \frac{dQ}{dT}$ and all the other expressions for $n'h\nu$ will follow immediately from the second law of thermodynamics.

The general expression for $n'N/h\nu$ at T is

$$\begin{aligned} n'N/h\nu &= n_0N/h\nu + T\left(\frac{n_1}{T_1} + \frac{n_2}{T_2} + \dots + \frac{n_T}{T}\right)N/h\nu \\ &= n_0N/h\nu + T \int_0^T \frac{dT}{T^2} \int_0^T \bar{C}_v dT, \end{aligned} \quad (16)$$

where \bar{C}_v is the mean molecular energy increment of the substance between 0° and T° and $n_1N/h\nu, n_2N/h\nu, \dots$ are real molecular energy increment at the respective temperatures as already described.

And the radiant density of $n'h\nu$ of the system is

$$\begin{aligned} \bar{D} &= \frac{8\pi h\nu^3 n^3}{c^3} \times e^{-\frac{h\nu}{kT}} \times \frac{e^{-\frac{n'h\nu}{kT}}}{e^{-\frac{h\nu}{kT}}} = \frac{8\pi h\nu^3 n^3}{c^3} e^{-\frac{n'h\nu}{kT}} \\ &= \frac{8\pi h\nu^3 n^3}{c^3} e^{-\frac{n'N/h\nu}{RT}} = \frac{8\pi h\nu^3 n^3}{c^3} e^{-\frac{n_0N/h\nu}{RT}} - \int_0^T \frac{dT}{RT^2} \int_0^T \bar{C}_v dT, \end{aligned} \quad (17)$$

then

$$k_1 = P\Pi N\varepsilon \frac{8\pi h\nu^3 n^3}{c^3} e^{-\frac{n_0N/h\nu}{RT}} - \int_0^T \frac{dT}{RT^2} \int_0^T \bar{C}_v dT. \quad (18)$$

If we put

$$\Pi \frac{8\pi h\nu^3 n^3}{c^3} = \Pi\pi,$$

then

$$\ln k_1 = \ln P + \Sigma \ln N\varepsilon + \Sigma \ln \pi - \sum \frac{n_0N/h\nu}{RT} - \sum \int_0^T \frac{dT}{RT^2} \int_0^T \bar{C}_v dT. \quad (19)$$

And we can get a similar expression for $\ln k_2$.

Then

$$\ln K = \frac{Q_0}{RT} - \Sigma \int_0^T \frac{dT}{RT^2} \int_0^T \bar{C}_v dT + \Sigma \mathcal{E}.$$

Now from the relation (12), we get

$$\ln K = -\frac{Q_0}{RT} - \Sigma \int_0^T \frac{dT}{RT^2} \int_0^T C_v dT + \Sigma \mathfrak{C}. \quad (20)$$

This is the expression of the affinity constant of a reaction and it is the same as that derived from Nernst's theorem where, C_v is the mean molecular heat and $\mathfrak{C} = \ln N\varepsilon + \ln \pi$, chemical constant of a reacting substance.

Strictly, therefore, the chemical constant of a substance is not the real constant in different systems, but it depends upon the index of refraction of its radiation in a system where the substance is found. O. Sackur¹ has found the expression of chemical constant as a simple function of a atomic weight from a standpoint of entropy expression. In our case, the expression of an elemental sphere of a reaction ε is not yet known, but probably, it is not impossible to get its expression as a simple function of ν , or an atomic number.

In conclusion, the author wishes to express his cordial thanks to Professor M. Katayama of Tōhoku University for his valuable advice.

¹ Nernst Festschrift, 405, (1912)