A Quantum-Mechanical Consideration of Chemical Reaction Rates

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Introduction

As is well known, the statistical-mechanical theory of reaction rates (the absolute reaction rate theory or the ARR theory)[1] is very useful for the evaluation of reaction rates. However, apart from the knowledge of interaction potential of the reacting system, the theory also includes some imperfect points which have been often the subjects of discussion. These points are as follows: First, the motion of a mass point representing the reacting system along the reaction path is treated classical-mechanically and the concept of the "activated complex" is used even if its existence is doubtful. Second, the thermal equilibrium between the initial and activated states, or more rigorously, the reacting system in equilibrium is postulated. As a correction for these simplifications, the transmission coefficient κ is introduced, but its value cannot be determined from the theory itself.

The equilibrium postulate and then the statistical-mechanical property of κ must be discussed from the standpoint of non-equilibrium theory and several researches have been done previously[2], while the stability of the complex and the classical approximation of the motion are to be considered on the basis of quantum theory, so that the quantum-mechanical property of κ may be given.

In principle, the problem of the usual chemical reaction involving an activation energy can be treated as the quantum-mechanical transmission of a mass point representing the reacting system through an energy barrier occurring in the mutual potential field of the system[3–8].

Though this procedure has the great advantage of getting a rate equation without the concepts as stated above and of giving the definite probabilities of transitions from the initial to the final states, it has been applied only for one-dimensional problems except in a few works[5].

To examine, therefore, the validity of the ARR theory, it will be necessary to compare the ARR equation with the equation derived by this procedure for the same potential barrier which is like an actual one.

In this paper a rate equation will be derived by use of the more natural potential form than those used by others and some theoretical considerations about the quantum-mechanical property of the transmission coefficient and the validity of the ARR theory will be made on the basis of this equation.

Transmission through a Simplified Two-dimensional Potential Energy Barrier.

In this section we treat, as a typical example, the reaction between an atom A and a molecule BC in a linear configuration which involves an activation energy. Since there is scarcely any reaction for which the precise feature of the potential energy surface is known, we may assume a simple form of potential barrier from two plausible restrictions as follows:

a) When an atom A approaches to a molecule BC on a straight line (Fig. 1), the minimum of the potential energy is obtained where the interatomic distance of BC is equal to its equilibrium value[9].

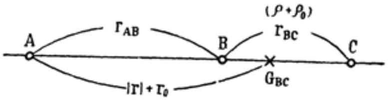

Fig. 1. Coordinate system.

b) In the vicinity of the barrier the vibrational potential differs slightly from the initial one of the molecule BC.

On these bases and by taking the coordinate system r and ρ defined by

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[1] See, for example, S. Glasstone, K.J. Laidler and H. Eyring, "The Theory of Rate Processes", McGraw-Hill Book Co. Inc., New York, 1941, Chap. IV p. 184. The more rigorous discussion has been given by J. Horiuti, This Bulletin, **13**, 210 (1938).

[2] B.J. Zwolinski and H. Eyring, *J. Am. Chem. Soc.*, **69**, 2702 (1947); I. Prigogine, *J. phys. & Colloid. Chem.*, **55**, 765 (1951).

[3] E. Wigner, *Z. physik. Chem.*, B **19**, 203 (1932).

[4] R.P. Bell, *Proc. Roy. Soc.*, A **139**, 466 (1933).

[5] For example, J.O. Hirschfelder and E. Wigner, *J. Chem. Phys.*, **7**, 616 (1939).

[6] E. Bauer and Ta-You Wu, *J. Chem. Phys.*, **21**, 726 (1953).

[7] F.A. Matsen, *J. Chem. Phys.*, **22**, 165 (1954).

[8] Also see, H. Eyring, J. Walter and G.E. Kimball, "Quantum Chemistry", John Wiley and Sons, Inc., New York, 1949, Chap. XVI p. 299.

[9] In this case, therefore, the reaction path has no curvatures which cause the transfer of energy between several degrees of freedom. Reactions with such a straight reaction path near the barrier are known from the calculations by the semi-empirical method. See, for example, Ref. 1), Chap. V p. 202.

$$-r+r_0=r_{AB}+(m_C/(m_B+m_C))r_{BC} \qquad (1)$$

and
$$\rho+\rho_0=r_{BC}, \qquad (2)$$

respectively, where r_0 and ρ_0 are the coordinates of the top of the barrier (the activated state), we assume the following simple two-dimensional potential surface as shown in Fig. 2 and its analytical expression to be

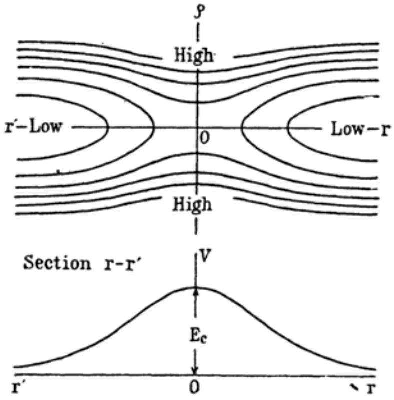

Fig. 2. Potential energy barrier.

$$V(r,\ \rho)=V_r(r)+(a_0-aV_r(r))\rho^2, \qquad (3)$$

where a_0 and a are constants. Then, $aV_r(r)\rho^2$ is the deviation from the vibrational potential $a_0\rho^2$ which corresponds to that of the molecule BC, and vanishes as r becomes indefinitely large[10].

Separating the equation for the motion of the center of mass, the wave equation of the system is expressed by

$$-\frac{h^2}{8\pi^2 M}\left(\frac{\partial^2}{\partial X^2}+\frac{\partial^2}{\partial Y^2}+\frac{\partial^2}{\partial Z^2}\right)\chi(X,Y,Z) =E_G\cdot\chi(X,Y,Z) \qquad (4)$$

and

$$\left[-\frac{h^2}{8\pi^2\mu}\frac{\partial^2}{\partial r^2}-\frac{h^2}{8\pi^2 m}\frac{\partial^2}{\partial\rho^2}+V(r,\rho)\right] \times\psi(r,\rho)=E_i\cdot\psi(r,\rho), \qquad (5)$$

where M is the sum of m_A, m_B and m_C, masses of each atom, m and μ are the reduced masses,

$$m=m_Bm_C/(m_B+m_C)$$

and
$$\mu=m_A(m_B+m_C)/M, \qquad (6)$$

respectively, X, Y and Z are the coordinates of the center of mass of the system, E_G and E_i are the energies of the translational motion of the whole system and of the internal motion of the system, respectively.

Eq. (4) can be solved immediately under some boundary conditions. To solve Eq. (5), one expands $\psi(r,\rho)$ in the following form

$$\psi(r,\rho)=\sum_n\psi_n(\rho)\cdot F_n(r) \qquad (7)$$

where $\psi_n(\rho)$ is the n-th normalized eigenfunction for the harmonic oscillator and satisfies the following equation

$$\left[-\frac{h^2}{8\pi^2 m}\frac{d^2}{d\rho^2}+a_0\rho^2\right]\psi_n(\rho)=E_n\psi_n(\rho). \qquad (8)$$

Substituting Eq. (7) in Eq. (5) and multiplying both sides of Eq. (5) by the complex conjugate of $\psi_n(\rho)$, $\psi_n{}^*(\rho)$, and integrating over ρ, one obtains

$$\left[\frac{h^2}{8\pi^2\mu}\frac{d^2}{dr^2}+E_t-V_r(r)(1-a\rho^2_{nn})\right]F_n(r) =-aV_r(r)\left[\rho^2_{n,n-2}F_{n-2}(r)+\rho^2_{n,n+2}F_{n+2}(r)\right] \qquad (9)$$

$$n=0,1,2,\cdots\cdots,$$

where
$$E_t=E_i-E_n \qquad (10)$$

and
$$\rho^2_{kl}=\int_{-\infty}^{+\infty}\psi_k{}^*(\rho)\rho^2\psi_l(\rho)d\rho. \qquad (11)$$

This set of simultaneous differential equations can not be solved rigorously. However, if $a\rho^2_{kl}$ $(k=n,\ l=n,\ n\pm 2)$ is sufficiently small compared with unity[11], we may take, as zero-order approximation, the right-hand side of Eq. (9) to be zero. Then it is separated into the uncoupled equations and is expressed by the single term functions, $\psi_n(\rho)F_n(r)$, i.e.,

$$\left[\frac{h^2}{8\pi^2\mu}\frac{d^2}{dr^2}+E_t-V_r(r)(1-a\rho^2_{nn})\right]F_n(r)=0, \qquad (12)$$

$$n=0,1,2,\cdots\cdots.$$

Since the above equations are those for one-dimensional problems in which the potentials are given by $V_r(r)(1-a\rho^2_{nn})$, if an analytical $V_r(r)$ with the shape like that shown in Fig. 2 is adopted, we can get its solution.

As a form of $V_r(r)$, for example, we may take the Eckart potential,

$$V_r(r)=E_c/\cosh^2(\pi r/l). \qquad (13)$$

Then Eq. (12) can be solved by the manner quite analogous to Eckart's original work[12] and the approximate solutions of Eq. (5) are derived as follows:

$$\psi(r,\rho)=\psi_n(\rho)\cdot F_n(r),\quad n=0,1,2,\cdots\cdots \qquad (14)$$

$$\psi_n(\rho)=N_nH_n(\sqrt{\beta}\cdot\rho)e^{-\frac{\beta}{2}\rho^2}, \qquad (15)$$

where $\beta=(2ma_0)^{1/2}/\frac{h}{2\pi}$ and

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[10] Since r_{AB} is always larger than zero, a potential of this type becomes inadequate at $r>0$. But such an approximation as this is necessary to simplify the form of the solution of Eq. (5) at $r\ll 0$.

[11] This condition also means that $aV_r(r)$ is much smaller than a_0.

[12] C. Eckart, *Phys. Rev.*, **35**, 1303 (1930). Also see Ref. 8).

$$\begin{aligned}F_n(r)&=a_1F_{n1}(r)+a_2F_{n2}(r)\\&=a_1(-\xi)^{i\alpha_n}F\{1/2+i\delta_n,\ -1/2-i\delta_n,\\&\quad 1+2i\alpha_n,\ \xi/(\xi-1)\}\\&\quad+a_2(-\xi/(1-\xi)^2)^{-i\alpha_n}F\{1/2+i\delta_n-2i\alpha_n,\\&\quad -1/2-i\delta_n-2i\alpha_n,\ 1-2i\alpha_n,\ \xi/(\xi-1)\},\end{aligned}\tag{16}$$

where N_n is the normalizing factor for the n-th eigenfunction for Eq. (8) and $H_n(\sqrt{\beta}\cdot\rho)$ is the Hermite polynomial of the n-th order and $F(r)$ is the hypergeometric function, in which ξ is a variable, $\xi=-\exp(2\pi r/l)$ and

$$\alpha_n=1/2(E_t/C)^{1/2},\tag{17}$$

$$\delta_n=[E_c(1-a\rho_{nn}^2)/C-1/4]^{1/2},\tag{18}$$

$$C=h^2/8\mu l^2.\tag{19}$$

At $r=-\infty$, $F_{n1}(r)$ and $F_{n2}(r)$ correspond to an incident and reflected waves of unit amplitude respectively and the ratio of their coefficients a_2/a_1 is determined uniquely by giving the condition that a transmitted wave only exists at $r=+\infty$ (Appendix I). Consequently, the transmission coefficient κ_{nn} is given by

$$\kappa_{nn}=1-\ \frac{a_2}{a_1}\ {}^2=\frac{\cosh(4\pi\alpha_n)-1}{\cosh(4\pi\alpha_n)+\cosh(2\pi\delta_n)},\tag{20}$$

since δ_n is real in this case. Further, when α_n and δ_n are much larger than zero, one may take

$$\kappa_{nn}\simeq\exp(4\pi\alpha_n)/[\exp(4\pi\alpha_n)+\exp(2\pi\delta_n)]\tag{21}$$

as an approximate formula.

Eq. (20) for κ_{nn} gives immediately its dependence on the relative momentum along the reaction path, $p_r=(2\mu E_t)^{1/2}$ and this has been discussed by Bell[4] previously.

Here we confine ourselves to its dependence on the vibrational potential. Differentiating κ_{nn} with respect to a, one can easily find

$$\frac{\partial\kappa_{nn}}{\partial a}=\frac{2\pi E_c\rho_{nn}^2\sinh^2(2\pi\alpha_n)\sinh(2\pi\delta_n)}{\delta_nC[\cosh(4\pi\alpha_n)+\cosh(2\pi\delta_n)]^2}\geqq 0.\tag{22}$$

This means that κ_{nn} increases or decreases according as the curvature of the vibrational potential at the barrier becomes smaller or larger. Also this property of κ_{nn} corresponds to the dependence of the reaction rate on the variation of the zero-point vibrational energy of the "activated complex" in the ARR theory (Fig. 3).

This relationship will be elucidated after we shall have formulated the rate equation based on κ_{nn}. If $a\rho_{k1}^2$ is not so small as assumed above, not only the transitions between the initial and final states with the same vibrational quantum number, but also the transitions between the states which differ by two quantum number become appreciable. A modified treatment for this case is shown in Appendix I.

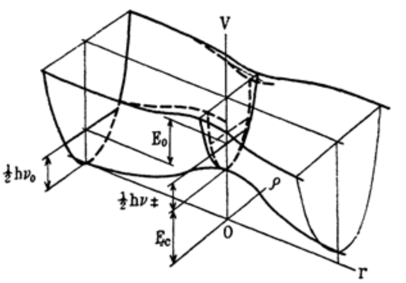

Fig. 3. Energy levels on potential surface.

Rate Equation on the Basis of the Transmission Coefficient and its Comparison with the ARR Equation for the Reaction $H+H_2\rightarrow H_2+H$

To obtain a rate equation, it is necessary to sum over the transmission of all the systems weighted by the energy distribution. Now, let $N(\boldsymbol{p}_G,\ p_r,\ n)$ be the number of the systems which exist in the volume element $d\boldsymbol{R}=dX\cdot dY\cdot dZ$ and in the width dr of the initial region far from the barrier, with the momentum of the center of mass $\boldsymbol{p}_G\sim\boldsymbol{p}_G+d\boldsymbol{p}_G$, the relative momentum along the reaction path $p_r\sim p_r+dp_r$ and the vibrational quantum number n.

$$N(\boldsymbol{p}_G,\ p_r,\ n)=N_0(\boldsymbol{p}_G,\ p_r,\ n)\frac{d\boldsymbol{p}_Gd\boldsymbol{R}}{h^3}\cdot\frac{dp_rdr}{h},\tag{23}$$

where $N_0(\boldsymbol{p}_G,\ p_r,\ n)$ is the density whose expression in thermal equilibrium is given by Appendix II Eq. (A, 13). The number of the systems moving towards the barrier in unit time is $Np_r/\mu dr$; moreover, only a fraction $\kappa_n=\sum\limits_j\kappa_{nj}$ of them reacts and attains to the final states j. Accordingly, the reaction velocity v can be written as follows:

$$\begin{aligned}v=k(A)(BC)&=\frac{1}{h^3}\iiint\sum_n\sum_j\kappa_{nj}\\&\quad\times N_0(\boldsymbol{p}_G,\ p_r,\ n)\frac{p_r}{\mu h}\cdot dp_rd\boldsymbol{p}_Gd\boldsymbol{R},\end{aligned}\tag{24}$$

where (A) and (BC) are the concentrations of the atom A and the molecule BC respectively, and k is the rate constant. Assuming the initial systems in thermal equilibrium[13], and using the approximate formula of κ_{nn} shown in Eq. (21), one can obtain the rate constant

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[13] The consideration about the statistical-mechanical property of κ is not given here. However the non-equilibrium effect is expected to be small. (See Ref. 2).

$$k=\frac{kT}{h}\,\frac{f^{+}_{+tr.}}{F_{\mathrm{A}}\cdot F_{\mathrm{BC}}}\exp\left(\frac{h\nu_0}{2kT}\right)\sum_{n}\left[1+2\sum_{m=1}^{\infty}\left\{(C/4\pi^2kT)^m\cdot L_{2m}(x_n)\cdot\sum_{p=1}^{\infty}\frac{(-1)^p}{p^{2m}}\right\}\right]\exp\left(-y_n^2\right), \tag{25}$$

where

$$L_{2m}(x_n)=-\left[\exp\left(x^2\right)\frac{d^{(2m)}}{dx^{(2m)}}\exp\left(-x^2\right)\right]_{x=x_n}, \tag{26}$$

$$x_n^2=\frac{1}{kT}\left[E_c-h\left(\frac{\nu_0{}^2-\nu^{+2}_{+}}{2\nu_0}\right)\cdot\left(n+\frac{1}{2}\right)-C/4\right] \tag{27}$$

and

$$y_n^2=x_n^2+\frac{h\nu_0}{kT}\left(n+\frac{1}{2}\right).$$

Derivation of Eq. (25) is shown in Appendix II. In the equation (25), $f^{+}_{+tr.}$ is the partition function per unit volume for the translational motion of the whole system and also of the "activated complex" and F_{A} and F_{BC} are the partition functions per unit volume of the atom A and the molecule BC defined by the usual manner of the rate theory excluding only the term for the rotational motion[1]. ν_0 and ν^{+}_{+} are the vibrational frequencies deduced from the relations

$$a_0=2\pi^2m\nu_0^2 \quad\text{and}\quad a_0-aV_r(0)=2\pi^2m\nu^{+2}_{+} \tag{29), (30}$$

respectively.

The rate constant Eq. (25) formally reduces to that of the ARR theory in the case where $C/4\pi^2kT$ approaches to zero; that is, in the reaction involving heavy particles and a broad potential barrier at high temperatures, i.e.,

$$k=\frac{kT}{h}\,\frac{f^{+}_{+tr.}}{F_{\mathrm{A}}\cdot F_{\mathrm{BC}}}\left[1-\exp\left(-\frac{h\nu_a}{kT}\right)\right]^{-1}\times\exp\left[-\frac{1}{kT}\left(E_c+\frac{1}{2}h\nu_a-\frac{1}{2}h\nu_0\right)\right]. \tag{31}$$

It should be noted, however, that the term corresponding to the vibrational partition function of the "activated complex" in the ARR theory includes the average frequency $\nu_a=(\nu_0^2+\nu^{+2}_{+})/2\nu_0$ instead of ν^{+}_{+}. Here it is interesting to estimate the degree of deviation of the ARR theory from the equation derived above. Since the ARR equation for the same reaction between an atom A and a molecule BC of linear configuration, is given by Eq. (31), if ν^{+}_{+} is adopted instead of ν_a, i.e.,

$$k_{\mathrm{A}}=\frac{kT}{h}\cdot\frac{f^{+}_{+tr.}}{F_{\mathrm{A}}\cdot F_{\mathrm{BC}}}\left[1-\exp\left(-\frac{h\nu^{+}_{+}}{kT}\right)\right]^{-1}\times\exp\left[-\frac{1}{kT}\left(E_c+\frac{1}{2}h\nu^{+}_{+}-\frac{1}{2}h\nu_0\right)\right], \tag{32}$$

the ratio of k_{A} to k is easily given by Eqs. (25) and (32). As an example, we have calculated this deviation for the reaction $H+H_2\rightarrow H_2+H$ for which the largest quantum effect may be expected. The results are shown in Table I. In the table, $(k_{\mathrm{A}}/k)_1$ are the values for the measure of width of the barrier $l=3.65\,A$, for which the curvature along the reaction path at the top of the barrier is equal to that obtained by the semi-empirical calculation[14], and $(k_{\mathrm{A}}/k)_2$ are the values for $l=1.15\,A$. For other constants, $h\nu_0=12.56$, $h\nu^{+}_{+}=10.36$ and $E_c=7.63$ kcal./mol. are adopted in both calculations. The differences between both results are not very large except in the cases of small l at low temperatures.

TABLE I

RATIO OF CALCULATED RATES FOR THE REACTION

$H+H_2\rightarrow H_2+H$

Temp. °K	300	500	1000	2000
$(k_A/k)_1$	0.974	1.029	1.030	1.022
$(k_A/k)_2$	0.193	0.574	0.873	0.971

Discussion

It seems that the result of comparison in the previous section leads to the conclusion that the ARR theory gives a fairly good approximation for usual chemical reaction rates at high temperatures. However, since our equation has been derived on several approximations and restrictions, it is necessary to examine them to confirm the conclusion. One of the approximations is that the Eckart type potential barrier which is perhaps steeper than the actual one near the top has been used. Therefore, we have calculated the rates for the two potentials with different l, so that the actual case may be between them. Though the results depend strongly on the choice of l at low temperatures, as the temperature rises, both results come to be in accord with each other and this fact suggests the behavior in the actual potential. The potential of this type seems to be the most precise form that can be used at present. Another approximation we have made is the use of the single term wave function valid when $a\rho_{kl}^2$ is very small. Since $a\rho_{nn}^2$, for in-

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[14] J.O. Hirschfelder, H. Eyring and B. Topley, *J. Chem. Phys.*, 4, 170 (1936).

stance, is expressed as $a\rho_{nn}^2 = h(\nu_0^2 - \nu_+^{+2})(n+1/2)/2E_c\nu_0$, it increases with n, so that the condition $1 \gg a\rho_{nn}^2$ loses its validity for certain large n and, then, the cross transitions between the states with n and $n \pm 2$ become appreciable. For this case, the method of distorted waves is applied and the equation for the transmission coefficient κ_n including cross transitions is derived. The details are shown in Appendix I. But it is quite laborious to obtain the numerical value of κ_n because of the complicated functions F_n and $F_{n\pm2}$. However, in the case of usual reactions involving the molecule of low vibrational frequency, it may safely be said that the condition, $E_c \gg h\nu_0 \gg h(\nu_0 - \nu_+^+)$, holds. Then the rate constant Eq. (25), except at very high temperatures, will converge rapidly for the summation over n with the restriction $1 \gg a\rho_{kl}^2$, since the concentrations of the reacting system of high energies decrease rapidly because of the Boltzmann factor. On the other hand, it is easily found from the properties of the matrix elements ρ_{kl}^2 that the set of equations (9) can be divided into two groups according as the vibrational quantum number n is even or odd. So, in the case of hydrogen atom-molecule reaction, if we put the restriction on energy, $E_{n=2} > E_i$, $\psi_0(\rho)F_0(r)$ and $\psi_1(\rho)F_1(r)$ will become good approximations for $\psi(r, \rho)$, since $E_{n=2} \gg E_c + 1/2 \cdot h\nu_+^+$ and $h\nu_0 \gg kT$ are satisfied. In this case the summation in Eq. (25) is taken for $n=0, 1$ and a correction term, $-\exp(-E_{n=2}/kT)$, is added inside the summation, assuming $\kappa_n = 1$ for the systems with $E_i \geq E_{n=2}$.

By the way, it is easily shown that Eq. (25) for the rate constant includes Wigner's equation with a quantum correction[3)], as a special case. Expanding the potential, $V_r(r)$, Eq. (3), in power series of r and neglecting the higher terms than r^2, one obtains

$$V_r(r) = E_c(1 - (\pi r/l)^2) \tag{33}$$

and by use of this potential the vibrational frequency ν_t along the reaction path,

$$\nu_t^2 = \frac{1}{4\pi^2\mu}\left(\frac{d^2V_r(r)}{dr^2}\right)_{r=0} = -\frac{E_c}{2\mu l^2}. \tag{34}$$

In Eq. (25), if one takes the term $m=1$ only, the rate constant,

$$k \simeq \frac{kT}{h}\,\frac{f_{+tr.}^{+}}{F_{\mathrm{A}} \cdot F_{\mathrm{BC}}}\exp\left(\frac{h\nu_0}{2kT}\right)\sum_n\Bigg[1 + \frac{1}{24} \times \left(\frac{h}{kT}\right)^2 \frac{E_c}{2\mu l^2}(1 - \gamma_n)\Bigg] \cdot \exp(-y_n^2) \tag{35}$$

is obtained, where

$$\gamma_n = \frac{1}{E_c}\left\{h\left(\frac{\nu_0^2 - \nu_+^{+2}}{2\nu_0}\right)\left(n + \frac{1}{2}\right) + \frac{1}{4} + \frac{1}{2}kT\right\}. \tag{36}$$

Then, in the case where the conditions

$$1 \gg \gamma_n \text{ and } \nu_a \simeq \nu_+^+$$

hold, the above equation (35) reduces to the ARR equation with a correction term $1/24 \cdot (h\nu_t/kT)^2$, that is, Wigner's equation. Also our results are similar to those obtained by Hirschfelder and Wigner[5)] in several points, for example, the dependence of the transmission coefficient κ on the relative translational energy or on the vibrational potential. Their result for the persistence of the vibrational quantum number in the reaction, even if the difference between frequencies of the initial and final states is not small, suggests that the contribution of the cross transitions to κ is not so large in our case. However because of their potential form, as well as Matsen's[7)], with the abrupt change of height or of vibrational potential, the obtained κ is essentially of oscillating character with the relative momentum p_r, while in our case, it has not such a property as long as the condition $1 \gg a\rho_{nn}^2$ holds.

All the considerations above have been done on the basis of the two-dimensional case. It is quite difficult to assume the behavior of reaction in the many-dimensional case concerning several vibrational and rotational motions from the results in the present case.

But when the barrier is sufficiently broad and flat, it is expected that one may conveniently suppose the energy levels of the "activated complex", for example, the vibrational levels of frequency ν_a or more roughly of ν_+^+, (Eqs. (29) and (30)), which have width occurring from the short lifetime of the complex. If the level spacings are larger than their width, it will be possible to describe the state of the "activated complex" by the quantized partition function for these levels. This approximation with an appropriate correction for the average transmission coefficient is still available as far as the levels retain their individualities. On the contrary, when the level spacing and the level width are comparable in their magnitude for several motions of the complex, for example, the lower energy states of rotational motions, such a simple approximation can not be adopted. As a step towards the many-dimensional case correlating to the above problem, the physical scattering of atoms from diatomic molecules has been investigated only by Zener and others[15], because of mathematical difficulty. It will, therefore, be necessary for more researches in this realm to be accumulated to elucidate the nature of chemical reactions completely.

Summary

The transmission coefficient for the simplified two-dimensional potential barrier has been obtained and its property depending on the curvatures of the barrier and other factors has been discussed. On the basis of this coefficient a quantum-mechanical rate equation has been formulated, the limiting forms of which formally reduce to the ARR equation and to Wigner's equation including a quantum correction. Then the rate constants given by the equations in the present and the ARR theory have been compared for the reaction $H+H_2 \rightarrow H_2+H$.

It has been found, from the above results, that the classical approximations in the ARR theory are generally valid except the reactions involving light particles and a thin barrier at low temperatures.

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Appendix I

Formulation of a Modified Transmission Coefficient by the Method of Distorted Waves

To solve the coupled equations (9), we have taken the right-hand side of them to be zero as zero-order approximation. A further improvement can be made by solving the equations which include the solutions $F^0_{n\pm2}(r)$, obtained from the zero-order approximate equations (12), in their right-hand side. The general solution of such a heterogeneous differential equation is easily written as follows[16]:

$$F_n(r)=F^0_n(r)+F_{n2}(r)\int_{+\infty}^{r}F_{n3}(r)W(r)dr+F_{n3}(r)\times\int_{r}^{-\infty}F_{n2}(r)W(r)dr, \qquad (A, 1)$$

where

$$W(r)=-\frac{8\pi^2\mu a V_r(r)}{h^2}[\rho^2_{n,n-2}F^0_{n-2}(r)+\rho^2_{n,n+2}F^0_{n+2}(r)], \qquad (A, 2)$$

considering its property at two boundaries, $r\rightarrow\pm\infty$. In Eq. (A, 1), $F_{n2}(r)$ and $F_{n3}(r)$ are taken as two independent solutions of the homogeneous equation (12) and

$$F_{n3}(r)=gF^0_n(r), \qquad (A, 3)$$

where $F^0_n(r)$ is also the solution of the same equation and is given by Eq. (16), i.e.,

$$F^0_n(r)=F_{n1}(r)+\frac{a_2}{a_1}F_{n2}(r). \qquad (A, 4)$$

The coefficient g is determined from the condition

$$F_{n3}(r)\frac{dF_{n2}(r)}{dr}-F_{n2}(r)\frac{dF_{n3}(r)}{dr}=1. \qquad (A, 5)$$

Since $F_{n1}(r)$ and $F_{n2}(r)$ approach to $\exp(2\pi ir/\lambda)$ and $\exp(-2\pi ir/\lambda)$ respectively, as $r\rightarrow-\infty$, then

$$g=-\lambda/4\pi i, \quad \text{where} \quad \lambda=h/(2\mu E_t)^{1/2}, \qquad (A, 6), (A, 7)$$

is obtained. Substituting Eqs. (A, 3) and (A, 6) in Eq. (A, 1) and considering the asymptotic form of $F_n(r)$ as $r\rightarrow-\infty$, the modified transmission coefficient κ_n is derived as follows:

$$\kappa_n=1-\left|\frac{a_2}{a_1}+\left(\frac{\lambda}{4\pi i}\right)\int_{-\infty}^{+\infty}F^0_n(r)\cdot W(r)dr\right|^2. \qquad (A, 8)$$

Introducing the detailed expression of $W(r)$, Eq. (A. 2), the integral in Eq. (A, 8) is written as

$$\int_{-\infty}^{+\infty}F^0_n(r)W(r)dr$$

$$=-\frac{8\pi^2 a\mu E_c}{h^2}\{\rho^2_{n,\,n-2}I_1+\rho^2_{n,\,n+2}I_2\}, \qquad (A, 9)$$

where

$$I_1=\int_{-\infty}^{+\infty}F^0_n(r)\cosh^{-2}(\pi r/l)F^0_{n-2}(r)dr \qquad (A, 10)$$

and

$$I_2=\int_{-\infty}^{+\infty}F^0_n(r)\cosh^{-2}(\pi r/l)F^0_{n+2}(r)dr. \qquad (A, 11)$$

The analytical expressions for $F^0_{n\pm2}(r)$ are given by the equations analogous to Eq. (A, 4) for $F^0_n(r)$.

Appendix II

Derivation of Equation for Rate Constant

From Eq. (24) the rate constant is expressed as follows:

$$k=\frac{1}{(A)(BC)}\times\Big[\frac{1}{h^3}\iiint\sum_n\sum_j\kappa_{nj}N_0(\boldsymbol{p}_G, p_r, n)\frac{p_r}{\mu h}dp_r d\boldsymbol{p}_G d\boldsymbol{R}\Big]. \qquad (A, 12)$$

Assuming the initial systems in thermal equilibrium, the density function, $N_O(\boldsymbol{p}_G, p_r, n)$, is given by

$$N_0(\boldsymbol{p}_G, p_r, n)$$

$$=\frac{(A)(BC)}{F_A\cdot F_{BC}}\cdot c^{\frac{h\nu_0}{2kT}}\cdot e^{-\frac{E_n}{kT}}\cdot e^{-\frac{p_r^2}{2\mu kT}}\cdot e^{-\frac{p_G^2}{2MkT}}. \qquad (A, 13)$$

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[15] C. Zener, *Phys. Rev.*, **37**, 556 (1931); C.F. Curtiss and F.T. Adler, *J. Chem. Phys.*, **20**, 249 (1952).

[16] See, for example, N.F. Mott and H.S.W. Massey, "The Theory of Atomic Collisions", Oxford: Clarendon Press, 1949, p. 106.

Substituting Eq. (A, 13) in Eq. (A, 12),

$$k=\frac{1}{\boldsymbol{F}_{\mathrm{A}}\cdot\boldsymbol{F}_{\mathrm{BC}}}\exp\left(\frac{h\nu_o}{2kT}\right)\cdot\left(\frac{1}{h^3}\iint e^{-\frac{p_{\mathrm{G}}{}^2}{2MkT}}d\boldsymbol{p}_{\mathrm{G}}d\boldsymbol{R}\right)$$

$$\times\left(\sum_n e^{-\frac{En}{kT}}\cdot\int_0^\infty\sum_j\kappa_{nj}e^{-\frac{p_r{}^2}{2\mu kT}}\cdot\frac{p_r}{\mu h}dp_r\right)\qquad(\mathrm{A},14)$$

is obtained. Since, in our approximation, κ_{nj} exists only for $n=j$, we obtain the following expression for the integral in Eq. (A, 14)

$$I=\int_0^\infty\kappa_{nn}(p_r,n)\cdot e^{-\frac{p_r{}^2}{2\mu kT}}\cdot\frac{p_r}{\mu h}dp_r$$

$$=2\frac{kT}{h}\int_0^\infty\kappa_{nn}(x,n)xe^{-x^2}dx,\qquad(\mathrm{A},15)$$

where $x=p_r/(2\mu kT)^{1/2}$.

Since this integral including the approximate κ_{nn}, Eq. (21), just corresponds to that occurring in the statistical-mechanical treatment of the Fermi-Dirac gas,[17] it is easily integrated in analogous way and the result is

$$I=\frac{kT}{h}\Big[1+2\sum_{m=1}^{\infty}\Big\{(C/4\pi^2kT)^m\cdot L_{2m}(x_n)$$

$$\times\sum_{p=1}^{\infty}\frac{(-1)^p}{p^{2m}}\Big\}\Big]\exp(-x_n^2),\qquad(\mathrm{A},17)$$

where

$$L_{2m}(x_n)=-\left[\frac{d^{(2m)}}{dx^{(2m)}}\exp(-x_2)\right]_{x=x_n}\cdot\exp(x_n^2),$$

and

$$x_n^2=\frac{1}{kT}[E_c(1-\alpha\rho_{nn}^2)-C/4].\qquad(\mathrm{A},19)$$

If we express $\alpha\rho_{nn}^2$ by use of ν_0 and $\nu_\ddagger$ defined by Eqs. (29) and (30), then Eq. (A, 19) becomes

$$x_n^2=\frac{1}{kT}\left[E_c-h\left(\frac{\nu_0{}^2-\nu_\ddagger{}^2}{2\nu_0}\right)\left(n+\frac{1}{2}\right)-\frac{C}{4}\right],\qquad(\mathrm{A},20)$$

since

$$\rho_{nn}^2=\int_{-\infty}^{+\infty}\psi_n^*(\rho)\rho^2\psi_n(\rho)d\rho=\frac{h}{8\pi^2m\nu_0}(2n+1).\qquad(\mathrm{A},21)$$

Noting the relations

$$E_n=h\nu_0(n+1/2)\qquad(\mathrm{A},22)$$

and

$$f_{+\mathrm{tr.}}^{+}=\frac{1}{h^3}\iint e^{-\frac{p_{\mathrm{G}}^2}{2MkT}}d\boldsymbol{p}_{\mathrm{G}}d\boldsymbol{R},\qquad(\mathrm{A},23)$$

in which the integration over $\boldsymbol{R}$ is carried out for unit volume, and substituting Eqs. (A, 17) and (A, 20) in Eq. (A, 14), we can get the final equation (25).

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[17] J. E. Mayer and M. G. Mayer, "Statistical Mechanics", John Wiley & Sons, Inc., New York, 1940, p. 381.