for the condition $\Phi_i = 0$. The experiments further show that in the stationary state eq 4 is obeyed by both alkali ion species if the mean activities of the salts are substitutes for the single ion activities. The ratio $(a_{\pm}''_{\mathrm{KCl}}/a_{\pm}''_{\mathrm{LiCl}})_{\mathrm{stat}}$ which will be attained in the stationary state can be calculated from the known electrolyte concentrations in the left cell compartment by eq 8. The experimentally determined and the predicted value agree within the limits of error of our concentration determination: $(a''_{\mathrm{KCl}}/a''_{\mathrm{LiCl}})_{\mathrm{stat}}$ experimentally, 0.95; calculated, 0.98. The mutual influence upon one another of the activity coefficient of the alkali ions is not taken into account in the calculation.

Acknowledgment. The author is indebted to Professor R. Schlögl for his interest in this work and many helpful discussions.

On the WKB[1a] Evaluation of Vibrational Transition Probabilities[1b]

Hyung Kyu Shin

Contribution from the Department of Chemistry, University of Nevada, Reno, Nevada. Received November 6, 1967

Abstract: A complete WKB evaluation of the vibrational transition probability per collison, P, is developed by using the saddle-point method. The final expression of P is applied to several interaction systems for which the "exact" quantum mechanical solutions are known. Both results become identical in the asymptotic limit.

The probability of energy transfer between translation and vibration has been discussed theoretically by a number of authors on both classical and quantum mechanical grounds.[2-4] Although various forms of the interaction $U(r)$, where r is the distance between centers of mass of the collision partners, were assumed in the calculation, only for a few interaction potentials explicit forms of the probability have been obtained. The probability $P(E)$ that the oscillator will undergo the transition $i \rightarrow j$ because of the collision with the incident particle may be calculated by the method of distorted waves or by the method of perturbed stationary states in quantum mechanical treatments.[2,5] In either case, the probability is given by the following expression

$$P(E) = \frac{8\mu\xi_{ij}^{2}}{\hbar^{2}\sqrt{E(E+\Delta)}}\left[\int_{0}^{\infty} F(r)\mathcal{R}_i(E,r)\mathcal{R}_j(E+\Delta,r)\,\mathrm{d}r\right]^{2} \qquad (1)$$

where ξ_{ij} is the matrix element of the displacement of the oscillator from its equilibrium position taken between the unperturbed initial and final states of the oscillator, Δ (>0) is the magnitude of the change in the oscillator's energy due to the transition, μ is the reduced mass of the collision partners, $F(r)$ is the perturbing force of the oscillator, and for any positive energy E the function $\mathcal{R}_i(E,r)$ is the well-behaved solution of the radial wave equation

$$\frac{\mathrm{d}^{2}\mathcal{R}_i(E,r)}{\mathrm{d}r^{2}} + \frac{2\mu}{\hbar^{2}}[E - U(r)]\mathcal{R}_i(E,r) = 0$$

which is normalized so that as $r \rightarrow \infty$, $\mathcal{R}_i(E,r) \sim \cos(\sqrt{2\mu E}r/\hbar + \delta_i)$. If we include the centrifugal potential energy, then $U(r)$ should be replaced by the effective potential $U(r) + \hbar^2(l + {}^1/_2)^2/2\mu r^2$.

By recognizing the Landau principle,[6,7] Widom[8] has evaluated the integral, I, in eq 1 by using the WKB semiclassical wave functions. However, in his work and also in Landau's original work, the evaluation of the preexponential part of I has not been properly subjected to a critical examination; *i.e.*, the preexponential part of $P(E)$ has not yet been determined in the WKB treatment. This situation is largely due to the fact that a direct calculation of the perturbation integral with respect to the semiclassical wave functions presents formidable difficulties. Such difficulties arise because the wave functions are exponential, and the integrand in the integral is large whereas the integral itself is an exponentially small quantity. Rapp[9] has also attempted to evaluate the integral with the WKB wave functions; since he did not eliminate the difficulties arising from the infinities in the wave functions at the classical turning points, no result was obtained in his work. Furthermore, these works considered a one-dimensional case which is of little practical interest. In the case of motion in a central field of force the general wave equation in spherical polar coordinates permits a separation of the variables. If the radial component of the motion is designated by $\mathcal{R}(r)/r$, the function $\mathcal{R}(r)$ is then the solution of the radial equation given above. Langer[10] showed the application of the WKB analysis to the radial equation and obtained the solutions which can be used to evaluate the integral.

---

(1) (a) G. Wentzel, H. A. Kramers, and L. Brillouin. (b)This work was carried out under Grant AFOSR-68-1354 from the U. S. Air Force Office of Scientific Research.

(2) N. F. Mott and H. S. W. Massey, "The Theory of Atomic Collisions," 3rd ed, Clarendon Press, Oxford, 1965, Chapter 13.

(3) T. L. Cottrell and J. C. McCoubrey, "Molecular Energy Transfer in Gases," Butterworth & Co., Ltd., London, 1961, Chapter 6.

(4) K. Takayanagi, *Advan. Atomic Mol. Phys.*, **1**, 149 (1965).

(5) B. Widom, *J. Chem. Phys.*, **27**, 940 (1957).

(6) L. Landau, *Physik. Z. Sowjetunion*, **1**, 81 (1932); **2**, 46 (1932); L. Landau and E. Teller, *ibid.*, **10**, 34 (1936).

(7) L. Landau and E. M. Lifshitz, "Quantum Mechanics," Pergamon Press, London, 1958, Chapter 7.

(8) B. Widom, *Discussions Faraday Soc.*, **33**, 37 (1962).

(9) D. Rapp, LMSC Report, 6-90-61-14, 1961; *J. Chem. Phys.*, **40**, 2813 (1964).

(10) R. E. Langer, *Phys. Rev.*, **51**, 669 (1937).

Salkoff and Bauer[11] reported use of this analysis in a numerical program for the calculation of the cross section for vibrational excitation of hydrogen molecules in the ground state.

In the present paper, we present the complete WKB calculation of $P(E)$ in a simple form that can be applied to many physically reasonable interaction potentials by means of the saddle-point method which was originated by Riemann[12] and developed by Debye.[13] We use Langer's radial functions to evaluate the integral. To test the validity of the present treatment, application of the final form of $P(E)$ is made to several cases in which the "exact" quantum mechanical solutions are known.

The wave functions obtained by employing the WKB approximation in the regions on both sides of the turning point are well known.[14] However, the integral I cannot be evaluated accurately merely by substituting such wave functions, because I is an exponentially small quantity whereas the integrand is very large so that a small error in the integrand will cause a serious deviation in the over-all value of $P(E)$. Langer showed[10] the following functions as the asymptotic solutions to the radial wave equation

$$\mathcal{R}_i(E,r) \sim c_i|Q_i(r)|^{-1/2}\exp\left[\int_{r_i}^{r} Q_i(r)\,\mathrm{d}r\right] \quad (2\text{-}1)$$

$$\mathcal{R}_j(E+\Delta,r) \sim c_j|Q_j(r)|^{-1/2}\exp\left[-\int_{r_j}^{r} Q_j(r)\,\mathrm{d}r\right] \quad (2\text{-}2)$$

where

$$Q_i(r) = \hbar^{-1}\sqrt{2\mu[U(r) - E]}$$

$$Q_j(r) = \hbar^{-1}\sqrt{2\mu[U(r) - (E + \Delta)]}$$

c_i and c_j are constants and r_i and r_j are the turning points. In the one-dimensional case Landau obtained[7] essentially identical forms regarding the coordinate as a complex variable and displaced the path of integration off the real axis into the upper half-plane. The displaced path of integration does not pass through the turning points near which the WKB approximation is inapplicable.

By substituting the functions in eq 1 we obtain

$$P_{\mathrm{WKB}}(E) \sim \frac{4(\xi_{ij}c_i'c_j')^2}{\hbar^2\sqrt{E(E+\Delta)}}\left[\int_0^\infty \mathrm{g}(r)\exp[\hbar^{-1}\mathrm{f}(r)]\,\mathrm{d}r\right]^2 \quad (3)$$

where $c_i' = \sqrt{\hbar}c_i$ and $c_j' = \sqrt{\hbar}c_j$

$$\mathrm{f}(r) = -\sqrt{2\mu}\left[\int_{r_j}^{r}\sqrt{U(r) - (E+\Delta)}\,\mathrm{d}r - \int_{r_i}^{r}\sqrt{U(r) - E}\,\mathrm{d}r\right] \quad (4)$$

$$\mathrm{g}(r) = F(r)/\{[U(r) - (E+\Delta)][U(r) - E]\}^{1/4} \quad (5)$$

Now, let us evaluate the asymptotic behavior of the integral as $\hbar \rightarrow 0$ by use of the saddle-point method, which is one of the most powerful techniques in asymptotics. We consider r to be a complex variable, and write the integral in the form

$$I = \int_\alpha^\beta \mathrm{g}(r)\exp[\hbar^{-1}\mathrm{f}(r)]\,\mathrm{d}r \quad (6)$$

The functions $\mathrm{g}(r)$ and $\mathrm{f}(r)$ are independent of $\hbar$, and they are analytic functions of r for all r in the simply connected region $\mathcal{R}$. Assume that there is a point $r^* \epsilon \mathcal{R}$ where $\mathrm{f}'(r^*) = 0$ and $\mathrm{f}''(r^*) \neq 0$; *i.e.*, r^* is a saddle point of $\mathrm{g}(r)\exp[\hbar^{-1}\mathrm{f}(r)]$.

If δ is a number independent of $\hbar$ with the condition $0 < \delta < \pi/4$, then we can find $\rho > 0$ such that there are two opposite sectors of the circle with center r^* and radius ρ, with apertures $\pi/2 - 2\delta$

(i) $0 < |r - r^*| < \rho$

$$\left|\arg(r - r^*) + \frac{\pi}{2} + \frac{1}{2}\arg \mathrm{f}''(r^*)\right| < \frac{\pi}{4} - \delta$$

(ii) $0 < |r - r^*| < \rho$

$$\left|\arg(r - r^*) - \frac{\pi}{2} + \frac{1}{2}\arg \mathrm{f}''(r^*)\right| < \frac{\pi}{4} - \delta$$

These sectors are symmetric with respect to the axis of the saddle point, in which $|\exp[\hbar^{-1}\mathrm{f}(r)]| < |\exp[\hbar^{-1}\cdot \mathrm{f}(r^*)]|$. Then, the difference between the real part of $\mathrm{f}(r)$ and $\mathrm{f}(r^*)$ is

$$\mathrm{re}\ \mathrm{f}(r) - \mathrm{re}\ \mathrm{f}(r^*) < -{}^1/_2|r - r^*|^2|\mathrm{f}''(r^*)|2\sin 2\delta + O(|r - r^*|^3)$$

since in both sectors $\arg[-(r - r^*)^2\mathrm{f}''(r^*)] < \pi/2 - 2\delta$.

Assume points $\alpha_1, \alpha_2, \ldots, \alpha_i, \ldots$ in sector i and $\beta_1, \beta_2, \ldots, \beta_i, \ldots$ in sector ii such that the integration path from α_i to β_i through the saddle point determines the essential contribution of the integral. Along the paths from α_j to α_i and β_i to β_j, where $i \neq j$, re $|\mathrm{f}(r) - \mathrm{f}(r^*)|$ has an exponentially small contribution of the order of $\exp(-\hbar^{-1}K)\exp[\hbar^{-1}\ \mathrm{re}\ \mathrm{f}(r^*)]$, because the real part of $\mathrm{f}(r) - \mathrm{f}(r^*)$ now has a negative upper limit $-K$.

The real part of $\hbar^{-1}\mathrm{f}(r)$ is monatonic along the path, and Laplace's method[15] may be used to evaluate the integral asymptotically. The asymptotic expansions of $\mathrm{g}(r)$ and $\mathrm{f}(r)$ needed in the application of the saddle-point method is the Taylor expansions around that point of the steepest path at which $\mathrm{re}[\hbar^{-1}\mathrm{f}(r)]$ is a maximum. By introducing $r = r^* + cz$, where $\alpha_i \leqslant z \leqslant \beta_i$ and c is a complex number with modulus 1 whose argument corresponds to the direction on the axis from sector i to ii, *i.e.*

$$c = \exp\left[\frac{\pi i}{2} - \frac{i}{2}\arg \mathrm{f}''(r)\right]$$

we can expand

$$\mathrm{f}(r) = \mathrm{f}(r^*) + {}^1/_2\mathrm{f}''(r^*)c^2z^2 + \cdots \quad (7)$$

When eq 7 is introduced into eq 6, we have

$$I = c\mathrm{g}(r^*)\exp[\hbar^{-1}\mathrm{f}(r^*)]\int_{\alpha_i}^{\beta_i}\exp[{}^1/_2\hbar^{-1}\mathrm{f}''(r^*)c^2z^2]\,\mathrm{d}z \quad (8)$$

---

(11) M. Salkoff and E. Bauer, *J. Chem. Phys.*, **29**, 26 (1958).

(12) B. Riemann, "Collected Works" (Gesammelte Mathematische Werke), 2nd ed, H. Weber, Ed., Dover Publications, New York, N. Y., 1953, pp 424–430.

(13) P. Debye, *Math. Ann.*, **67**, 535 (1909).

(14) See, for example, E. D. Kemble, "Quantum Mechanics," Dover Publications, New York, N. Y., 1958, p 90.

(15) A. Erdélyi, "Asymptotic Expansions," Dover Publications, New York, N. Y., 1956, pp 36–39.

Laplace's asymptotic method then results in

$$I \sim \sqrt{\frac{2\pi\hbar}{|\mathrm{f}''(r^*)|}}\, \mathrm{g}(r^*) \exp[\hbar^{-1}\mathrm{f}(r^*)] \tag{9}$$

In the function $\mathrm{f}(r^*)$, only the real part of the exponent, which is always negative, is of interest. The imaginary part gives only an unimportant phase factor. Hence, we could put for the exponent the absolute value, with the negative sign, of the real part of $\mathrm{f}(r^*)$ which is

$$\exp[\hbar^{-1}\mathrm{f}(r^*)] \sim \exp\left[-\frac{\sqrt{2\mu}}{\hbar}\,\mathrm{re}\left\{\int_{r_j}^{r^*}\sqrt{U(r) - (E + \Delta)}\,\mathrm{d}r - \int_{r_i}^{r^*}\sqrt{U(r) - E}\,\mathrm{d}r\right\}\right] \tag{10}$$

The final expression of $P(E)$ in the WKB treatment is then

$$P_{\mathrm{WKB}}(E) \sim \frac{8\pi(\xi_{ij}c_i'c_j')^2}{\hbar\sqrt{E(E + \Delta)}}\frac{\mathrm{g}^2(r^*)}{|\mathrm{f}''(r^*)|} \exp[2\hbar^{-1}\mathrm{f}(r^*)] \tag{11}$$

Since only the real part of $\mathrm{f}(r^*)$ is of interest, no particular reference to the complex behavior of r will be necessary. From eq 6, r^* is the saddle point of $\mathrm{g}(r)\cdot\exp[\hbar^{-1}\mathrm{f}(r)]$, but not of $\exp[\hbar^{-1}\mathrm{f}(r)]$. At small r (near the origin) the function $\mathrm{g}(r)$ is no longer a slowly varying coefficient of the exponential part, and it can significantly affect the determination of r^*. Then, r^* is the root of $\mathrm{f}'(r) + \hbar[\mathrm{g}'(r)/\mathrm{g}(r)] = 0$, where the prime signifies the differentiation with respect to r. In the region of strong interaction $U(r^*) \gg E$, while $E > \Delta$; then the leading term of $\mathrm{f}''(r^*)$ is

$$-\frac{\Delta}{2}\sqrt{\frac{\mu}{2}}\left[\frac{U'(r^*)}{U^{3/2}(r^*)}\right]$$

The function $\hbar^{-1}\mathrm{f}(r^*)$ can be expressed, by performing a binomial expansion, in the region of strong interaction[8,16]

$$\exp[\hbar^{-1}\mathrm{f}(r^*)] \sim \left[-\hbar^{-1}\sqrt{\mu/2}\sum_{n=1}^{\infty}\frac{\Delta^n}{n!}H^{(n-1)}(E)\right]$$

where

$$H(E) = \int_E^{\infty}\frac{(\mathrm{d}r/\mathrm{d}U)}{\sqrt{U(r) - E}}\,\mathrm{d}U$$

Since the inverse derivative $\mathrm{d}r/\mathrm{d}U$ in the region of strong interaction takes a general form of

$$\mathrm{d}r/\mathrm{d}U = -\sum_{i=0}^{\infty}a_iU^{-(N+i)} \tag{12}$$

where N is close to or equal to unity depending on the assumed form of $U(r)$ and a's are constant, we have

$$H(E) = -\sqrt{\pi}\sum_{i=0}^{\infty}a_i\frac{\Gamma(N + i - 1/2)}{\Gamma(N + i)}E^{1/2-N-i} \tag{13}$$

The $(n - 1)$st derivative of this function is

$$H^{(n-1)}(E) = -\sqrt{\pi}\sum_{i=0}^{\infty}\sum_{n=1}^{\infty}a_i\frac{(-1)^n\Delta^n}{n!}\frac{\Gamma(N + i + n - 3/2)}{\Gamma(N + i)} \times E^{3/2-N-i-n} \tag{14}$$

The full expression of $P_{\mathrm{WKB}}(E)$ is now finally, from eq 11 and 14

$$P_{\mathrm{WKB}}(E) \sim \frac{4\pi^2\sqrt{2\mu}}{\hbar\Delta}\xi_{ij}{}^2\left[\frac{U^{1/2}(r^*)F^2(r^*)}{|U'(r^*)|}\right] \times \exp\left[\frac{\sqrt{2\pi\mu}}{\hbar}\sum_{i=0}\sum_{n=1}a_i(-1)^n\Delta^n \times \frac{\Gamma(N + i + n - 3/2)}{n!\Gamma(N + i)}E^{3/2-N-i-n}\right] \tag{15}$$

where we introduced

$$\mathrm{g}(r^*) = \frac{F(r^*)}{U^{1/2}(r^*)}[1 + O(\hbar)]$$

and $c_i = (\pi\mu E/4\hbar^2)^{1/4}$ and $c_j = [\pi\mu(E + \Delta)/4\hbar^2]^{1/4}$.

In the above derivation we did not consider the role of the centrifugal potential. We assumed that the interaction potential depends only on r but not on its orientation; then no torques act to transfer angular momentum between the internal motions of the colliding molecules and their relative motion. Every collision will then be characterized by the quantum number l of the relative angular momentum, which has the same value throughout the collision process. Then, we have

$$Q_i(r) = \hbar^{-1}\sqrt{2\mu\left[U(r) + \frac{\hbar^2(l + 1/2)^2}{2\mu r^2} - E\right]}$$

$$Q_j(r) = \hbar^{-1}\sqrt{2\mu\left[U(r) + \frac{\hbar^2(l + 1/2)^2}{2\mu r^2} - (E + \Delta)\right]}$$

When these functions are introduced in the above procedure, the transition probability will then appear as a function of l (*i.e.*, the i sum in eq 15 includes the l-dependent term). We shall discuss this case below with a specific form of $U(r)$. It is thus obvious that eq 15 is actually the *s* wave formula.

We now consider several specific potentials for which the exact values of $P(E)$ are known.

In the region of strong interaction the attractive part of $U(r^*)$ and $F(r^*)$ in the preexponential part is insignificant compared to the repulsive part. The effect of this part is, of course, important in determining the probability of intermolecular energy transfer, but the effect is essentially controlled by the attractive energy terms in the exponent of eq 15. The wave functions always vary much more rapidly compared to the interaction potential itself at small r, and the effect due to the attractive force terms in the wave functions directly enters in the exponent of $P(E)$, whereas the effect in $F(r)$ in eq 1 and in $U(r)$ of the coefficients of the wave functions given by eq 2 enters in the preexponential part. Therefore, we neglect the attractive parts of both $U(r^*)$ and $F(r^*)$ in eq 15, but not those in the exponent due to the wave functions.[17] Then, for example, for both the purely repulsive exponential potential $U(r) = D\exp(-r/a)$ and the Morse potential $U(r) = D[\exp(-r/2a) - 2\exp(-r/2a)]$, the preexponential parts become identical with each other. Now, we derive the transition probability for these potentials. The distance r^* is found to be

$$r^* = -2a\ln\left\{\sqrt{\frac{2\mu}{D}}\frac{a\Delta}{\hbar}[1 + O(\hbar)]\right\} \tag{16}$$

---

(16) H. Shin, *J. Chem. Phys.*, **42**, 59 (1965).

(17) H. Shin, *ibid.*, **47**, 3302 (1967).

The difference in r^* for these two potentials appears only at the terms of $O(\hbar)$. By evaluating $U(r^*)$ and assuming $F(r^*) = U'(r^*)$, the preexponential part can therefore be obtained as $(4a\pi\mu\Delta/\hbar^2)^2\xi_{ij}^2[1 + O(\hbar)]$. If we assume the harmonic oscillator wave function for the oscillator's vibration, the $\xi_{ij} = \hbar/\sqrt{2M\Delta}$, where M is the reduced mass of the oscillator, so that the preexponential part is $8(\Delta/M)(\pi\mu a)/\hbar)^2\,[1 + O(\hbar)]$.

For the purely repulsive case, $N = 1$ and the coefficient a_0 is a, but all other a's are zero; thus, the complete expression for $P(E)$ in the WKB approximation is

$$P_{\mathrm{WKB}}(E) \sim \left(\frac{4a\pi\mu\Delta}{\hbar^2}\right)^2 \xi_{ij}^2 \times \exp\left\{-\frac{\sqrt{2\mu}a\pi\Delta}{\hbar\sqrt{E}}\left[-1\,\frac{\Delta}{2E} + O(E^{-2})\right]\right\} \quad (17)$$

The corresponding quantum mechanical result obtained by Jackson and Mott is,[18] with $\xi_{ij}^2 = \hbar^2/2M\Delta$

$$P_{\mathrm{QM}}(E) = 8\left(\frac{\Delta}{M}\right)\left(\frac{a\pi\mu}{\hbar}\right)^2 \frac{\sinh(2\pi k_1)\sinh(2\pi k_2)}{[\cosh(2\pi k_2) - \cosh(2\pi k_1)]^2} \quad (18)$$

where $k_1 = a(2\mu E)^{1/2}/\hbar$ and $k_2 = a[2\mu(E + \Delta)]^{1/2}/\hbar$. When we replace the hyperbolic functions by their corresponding exponential forms and expand them in a power series of Δ/E for $2\pi k_1 \gg 1$ and $2\pi k_2 \gg 1$, the quantum mechanical result reduces to eq 17.

For the Morse potential we also find $N = 1$ but $a_0 = a$, $a_{1/2} = -a\sqrt{D}$, $a_1 = 0$, $a_{3/2} = aD^{3/2}/2$, ... With these values we obtain, from eq 15

$$P_{\mathrm{WKB}}(E) \sim \left(\frac{4a\pi\mu\Delta}{\hbar^2}\right)^2 \xi_{ij}^2 \times \exp\left\{-\frac{\sqrt{2\mu}a\pi\Delta}{\hbar\sqrt{E}}\left[1 - \frac{2}{\pi}\sqrt{\frac{D}{E}} + \frac{2}{3\pi}\left(\frac{D}{E}\right)^{3/2} - \frac{\Delta}{2E} + O(E^{-2})\right]\right\} \quad (19)$$

Devonshire's quantum mechanical calculation of $P(E)$ for this potential with the harmonic oscillator matrix element resulted[19,20] in

$$P_{\mathrm{QM}}(E) = 8\left(\frac{\Delta}{M}\right)\left(\frac{\pi\mu a}{\hbar}\right)^2 \times \frac{\sinh(4\pi k_1)\sinh(4\pi k_2)}{[\cosh(4\pi k_2) - \cosh(4\pi k_1)]^2}\,\frac{(A_1 + A_2)^2}{A_1A_2} \quad (20)$$

where $A_1 = |\Gamma(-d + 2ik_1 + 1/2)|^2$, $A_2 = |\Gamma(-d + 2ik_2 + 1/2)|^2$, and $d = 2a\sqrt{2\mu D}/\hbar$. Although it is a tedious procedure, it can be shown that when we replace the γ functions by the corresponding exponential forms[20] and expand them in a power series of Δ/E for $4\pi k_1 \gg 1$ and $4\pi k_2 \gg 1$, eq 20 reduces to the WKB form given by eq 19.

The introduction of the centrifugal potential term in the exponential potentials considered above leads to some mathematical difficulties because the inverse derivative $\mathrm{d}r/\mathrm{d}U$ is not possible to obtain in closed form. However, for the Lennard-Jones (LJ) potentials, the introduction does not lead to such difficulties. Then, for the effective potential $U_{\mathrm{eff}}(r) = 4D[(\sigma/r)^{12} - (\sigma/r)^6] - \hbar^2(l + 1/2)^2/2\mu r^2$, where $U_{\mathrm{LJ}}(\sigma) = 0$, we find $N = 13/12$ and $a_0 = (4D)^{1/12}\sigma/12$, $a_{1/2} = -7a_0\sqrt{D}/6$, $a_1 = 13a_0D/72$, $a_{5/6} = (11/24)[a_0\hbar^2(l + 1/2)^2/\mu\sigma(4D)^{1/6}]$, $a_{3/2} = 665a_0D^{3/2}/1296$, ... The transition probability is derived as

$$P_{\mathrm{WKB}}^{\,l}(E) \sim \left(\frac{48\pi^2}{2432}\right)\left(\frac{D^{1/2}\mu^{3/2}\Delta^2}{\hbar^4}\right)\left(\frac{\mu}{2D}\right)^{5/14}\left(\frac{14\hbar\sigma^6}{\Delta}\right)^{2/7}\xi_{ij}^2 \times \exp\left\{-\frac{\sqrt{2\pi\mu}}{\hbar}\,\frac{\Gamma(7/12)}{\Gamma(1/12)}\,\frac{(4D)^{1/12}\Delta\sigma}{E^{7/12}} \times \left[1 - \frac{1}{72}\left(\frac{\Gamma(1/12)}{\Gamma(7/12)}\right)^2\sqrt{\frac{D}{E}} - \frac{7}{14}\left(\frac{\Delta}{D} - \frac{1}{3}\right)\frac{\Delta}{E} + O(E^{-2})\right] - \frac{5}{288}\,\frac{\Gamma(5/12)}{\Gamma(11/12)}\,\frac{\sqrt{2\pi\mu}\hbar\Delta(l + 1/2)^2}{(4D)^{1/12}\mu\sigma E^{17/12}}\right\} \quad (21)$$

where the superscript l refers to the l-dependent term in the exponent, and this expression may be called the "partial" transition probability; then the "total" transition probability is $P_{\mathrm{WKB}}^{\mathrm{total}} = \Sigma_l(2l + 1)P_{\mathrm{WKB}}^{\,l}$. Although use of the Lennard-Jones potential for the investigation of molecular energy transfer has been made by several authors,[21-23] no explicit form of $P_{\mathrm{QM}}(E)$ needed for the comparison with the WKB result has been reported.

The calculation of $P(E)$ for an inverse-power potential whose leading repulsive term is A/r^s with $s \leqslant 2$ requires special consideration, *i.e.*, the potentials which fail to vanish more rapidly than $1/r^2$ for large r. The reason, of course, is the mixing of the true interaction with the centrifugal potential, which does not occur in real molecular collisions. For this case, use of the binomial expansion applied above to calculate $\hbar^{-1}\mathrm{f}(r^*)$ should be avoided; instead we must directly integrate the original form which contains simple integrals, *e.g.*, for $s = 2$

$$-\frac{\sqrt{2\mu}}{\hbar}\left\{\int_{r_i}^{r^*}\sqrt{\frac{A}{r^2} - (E + \Delta)}\,\mathrm{d}r - \int_{r_i}^{r^*}\sqrt{\frac{A}{r^2} - E}\,\mathrm{d}r\right\}$$

where r^* is found to be $(2A/\mu)^{1/4}(\hbar/\Delta)^{1/2}$. These integrals can be easily solved as

$$\frac{1}{2}\ln[(E + \Delta)/E] - \frac{1}{2}(\Delta/Ay^{*2}) - \frac{1}{32}(\Delta/Ay^{*2})^2 - \cdots$$

where $y^* = 1/r^*$, so that the exponential part is

$$\exp\left\{\frac{\sqrt{2\mu A}}{\hbar}\ln[E/(E + \Delta)]\right\} = [E/(E + \Delta)]^{\sqrt{2\mu A}/\hbar}$$

If we include the centrifugal potential, then in this expression A is now replaced by $A + \hbar^2(l + 1/2)^2/2\mu$.

Assuming the perturbation force $F(r) = B/r^2$ rather than $U'(r)$, Widom and Bauer[24] obtained the following expression for $P(E)$ for $U(r) = A/r^2$ in the distorted wave approximation

$$P_{\mathrm{QM}}(E) = \left(\frac{\mu}{MA\Delta}\right)(\pi B)^2[E/(E + \Delta)]^{\sqrt{2\mu A}/\hbar} \quad (22)$$

---

[18] J. M. Jackson and N. F. Mott, *Proc. Roy. Soc.* (London), **A137**, 703 (1932).

[19] A. F. Devonshire, *ibid.*, **A158**, 269 (1937).

[20] Also, see R. T. Allen and P. Feuer, *J. Chem. Phys.*, 40, 2810 (1964).

[21] T. L. Cottrell and N. Ream, *Trans. Faraday Soc.*, **51**, 159 (1955).

[22] E. E. Nikitin, *Opt. i Spektroskopiya*, **6**, 141 (1959); *Opt. Spectry.* (USSR), **6**, 93 (1959).

[23] H. Shin, *J. Chem. Phys.*, **41**, 2864 (1964).

[24] B. Widom and S. H. Bauer, *ibid.*, **21**, 1670 (1953).

When we calculate eq 15 with this perturbation force, it is easy to show that the WKB treatment yields $P(E)$ identical with eq 22, verifying the general conclusion concerning the relation of the two theories. The transition probability for this case is very much different from those for the potentials considered above, that $P(E)$ for $U(r) = A/r^2$ decreases with the magnitude of the change in the oscillator's energy, but as a power rather than as the exponential of a power and that there is no naturally definable interaction range parameter such as a of the exponential potentials.

There are, of course, other potential functions for which such comparison can be made; however, from the above results it suffices to conclude that $P_{\mathrm{WKB}}(E)$ and $P_{\mathrm{QM}}(E)$ become identical when E is sufficiently larger than Δ. Therefore, the present analysis and its consequent formulas may be found to have at least the advantages of simplicity and of generality of method. The important steps in the present treatment are to formulate r^* and to choose an appropriate integration path in the saddle-point method for integrals. The former step is involved in the evaluation of both exponential and preexponential parts through $U(r^*)$ and $F(r^*)$, while the latter is only important in the evaluation of preexponential part.

For the one-dimensional case (for which the coordinate may now be represented by x), the exponential part of $P_{\mathrm{WKB}}(E)$ is identical with that of the three-dimensional case, but the preexponential part is somewhat different because the coefficients of Landau's wave function $\psi(x)$ and Langer's radial function $\mathcal{R}(r)$ are different. In Landau's original work, x^* is the singular point of $U(x)$ and the integration of $\exp[\hbar^{-1}f(x)]$ is affected along the path which circles x^* counterclockwise. In the present approach for the one-dimensional case, however, we should determine x^* from $f'(x^*) + \hbar[g'(x)/g(x^*)] = 0$, *i.e.*, the saddle point of $g(x)\exp\cdot[\hbar^{-1}f(x)]$, and parameterize the path by $x = x^* + c'z'$, where z' belongs to the closed interval $[\alpha_i', \beta_i']$. Here the primes signify the one-dimensional case. The contribution of the integral from α_i' to β_i' can then be evaluated by application of the Laplace method. Taking x^* to be the singular point of $U(x)$ would leave the exponential part of $P(E)$ identical with the present results in the asymptotic limit, but would make it impossible to find the preexponential part. (However, the one-dimensional case is trivial, and it is not intended to present its solution here.) Any complete theory of vibrational transitions due to molecular collision should give not only the exponential of $P(E)$, but also the appropriate preexponential part.

Acknowledgment. This work has begun at Cornell University under the direction of Professor B. Widom. The author wishes to thank Professor Widom for many stimulating discussions.

Temperature Dependence of Intermolecular Energy Transfer in Polar Molecules[1]

Hyung Kyu Shin

Contribution from the Department of Chemistry, University of Nevada, Reno, Nevada. Received November 6, 1967

Abstract: An expression is developed for the temperature dependence of the probability of vibration–translation energy transfer in polar molecules assuming the Morse-dipole–quadrupole interaction energy. The development is based on a perturbation method which is essentially an extended distorted wave treatment. The angle dependence of the interaction between the permanent charges on the collision pairs is explicitly considered by averaging the angle-dependent collision integral over all possible rotations of the dipoles. The final expression for the vibrational transition probability per collision is obtained as $P(T) = fP_0(T)$, where $P_0(T)$ is the transition probability that would apply in the zero dipole and quadrupole limits and f represents the effect of the permanent charges on the energy transfer. It is shown that $P(T)$ can decrease to a minimum and then increase in "a normal fashion" as temperature increases for very polar molecules with a small molecular diameter. This anomalous behavior is related to the preferred orientation of the colliding molecules at low temperatures (300–600°K). Numerical calculations show such behavior in H_2O and NH_3. In SO_2 and CH_3Cl the calculation shows a little change in $P(T)$ with T at 300–500°K. Rotational energy transfer is neglected throughout.

The temperature dependence of the probability of energy transfer $P(T)$ between translational and vibrational motions of molecules per collision has been discussed theoretically by a number of authors on both classical and quantum mechanical grounds.[2-4] They expressed the temperature dependence by the equation

$$P(T) = A(T)\exp\left[-\frac{3\chi}{kT} + \frac{D}{kT} + \frac{\Delta}{2kT}\right] \qquad (1)$$

$$\chi = [\sqrt{(m/2)}\,(\pi a\Delta kT/\hbar)]^{2/3}$$

where $A(T)$ is the preexponential part which is weakly temperature dependent, m is the reduced mass of the colliding molecules, Δ is the magnitude of the change in

---

(1) This work was carried out under Grant AFOSR-68-1354 from the U. S. Air Force Office of Scientific Research.

(2) K. F. Herzfeld and T. A. Litovitz, "Absorption and Dispersion of Ultrasonic Waves," Academic Press Inc., New York, N. Y., 1959, Chapter 7.

(3) T. L. Cottrell and J. C. McCoubrey, "Molecular Energy Transfer in Gases," Butterworth & Co., Ltd., London, 1961, Chapter 6.

(4) K. Takayanagi, *Advan. Atomic Mol. Phys.*, **1**, 149 (1965).