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 $P_{\text{WKB}}(E)$ and $P_{\text{QM}}(E)$ 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 $P_{\text{WKB}}(E)$ 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 $\exp[\hbar^{-1}\mathrm{f}(x)]$ is affected along the path which circles x^* counterclockwise. In the present approach for the one-dimensional case, however, we should determine x^* from $\mathrm{f}'(x^*) + \hbar[\mathrm{g}'(x)/\mathrm{g}(x^*)] = 0$, *i.e.*, the saddle point of $\mathrm{g}(x)\exp\cdot[\hbar^{-1}\mathrm{f}(x)]$, 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]

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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

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(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).

the molecule's internal energy due to the transition (for a one-quantum transition, $\Delta = h\nu$, where ν is the vibrational frequency in sec^{-1}), D is the depth of the potential energy minimum in the interaction, and a is the range parameter which occurs when the interaction potential as a function of distance r between centers of mass of the molecules is represented by an exponential form $\exp(-r/a)$. $\hbar$ and kT have their usual meaning. Actually eq 1 is the result for the spherically symmetric interaction $U(r) = \text{constant} \cdot \exp(-r/a)$. The correction term D/kT arose from a physical argument that the approaching molecules are "speeded up" in a potential well of the depth D.[5]

Simple repulsive potentials are useful for calculations of the collision properties of gases at high temperatures where the attractive forces are not important and the molecular interactions are governed by valence or exchange forces. However, it has been shown that the attractive forces contribute significantly to the energy-transfer process at ordinary temperatures.[6-9] For the Morse potential $U = D[\exp(-r/a) - 2\exp(-r/2a)]$, we showed that the temperature dependence of the transition probability by[9]

$$P(T) = A(T)\exp\left[-\frac{3\chi}{kT} + \frac{4\sqrt{D\chi}}{\pi kT} + \frac{16D}{3\pi^2 kT} + \frac{\Delta}{2kT}\right] \qquad (2)$$

where the second and third terms in the exponent represent the effect of the attractive energy $-2D\exp(-r/2a)$ of the Morse potential. If the colliding molecules strongly attract each other, these terms can play an important role in controlling the over-all energy-transfer process. Another well-known potential for the calculation is the "exp-6" function, which has been, for example, applied in the calculation of $P(T)$ in nitrogen and chlorine molecules by Takayanagi.[10] He concluded that the short-range repulsive force had the major effect in the transition; the attractive term, however, cannot be simply neglected, because it affects the slope of the repulsive part of the potential on which $P(T)$ depends sensitively. There are, of course, other intermolecular potential functions for which the probability could be calculated.[4,9]

For polar molecules, however, the two-term potentials such as the Lennard-Jones (LJ) and Morse functions are inadequate, and explicit account has to be taken of the interaction of the permanent charges on the colliding molecules. For HCl, de Wette and Slawsky[11] concluded that the dipole–dipole interaction is important. This type of interaction also is known to be important for other molecules such as sulfur dioxide[12] and CH_3Cl.[13-15] The interaction of the permanent charges on the molecules is strongly orientation dependent. Since the explicit angle dependence of the interaction makes calculations of transition probabilities excessively difficult, the above investigations used the angle-averaged potential (the Krieger function)

$$U = 4D[(\sigma/r)^{12} - (\sigma/r)^6] - 2d^2/r^3 \qquad (3)$$

i.e., the combination of the LJ(12-6) potential $U_{LJ}(r)$ and the angle-averaged dipole–dipole interaction energy, where $U_{LJ}(\sigma) = 0$ and $d = \mu^2/2D\sigma^3$, μ being the dipole moment. The Krieger potential has been used largely because calculations of $P(T)$ for angle-dependent potentials are very difficult, but even for this potential no explicit form of $P(T)$ has been reported. Although it considers the importance of the dipole–dipole interaction, the orientation dependence of the intermolecular energy transfer cannot be examined with this potential, since it is an orientation-averaged function. At ordinary temperatures, where the angle dependence of the interaction of permanent charges on molecules can be particularly important, we must start the calculation with an angle-dependent interaction energy.

The most outstanding property of intermolecular (vibration–translation) energy transfer in polar gases is that $P(T)$ for certain molecules decreases to a minimum from a large value and then increases in a normal fashion as the temperature increases.[16-18] Theoretical formulations as they have been developed so far are incapable of accounting for this kind of anomalous temperature dependence of $P(T)$. At low temperatures the colliding molecules can take preferentially a particular relative orientation which is favored for energy transfer. Therefore, we must take into account more rigorously in the calculation the angle dependence of the interaction of permanent charges; *i.e.*, we calculate $P(E,\text{angles})$, where E is the initial relative energy and the "angles" represents the relative orientation of the colliding molecules, before averaging over energies and angles.

The purpose of the present paper is to develop an expression for the temperature dependence of the probability of intermolecular energy transfer in polar molecules considering the angle-dependent dipole–dipole and dipole–quadrupole interactions. In order to calculate $P(T)$ it will be necessary to make specific assumptions about the interaction energy, the wave functions, and the introduction of spherical harmonics in calculating the collision integral. In section II the interaction energy will be assumed as a sum of the Morse potential, dipole–dipole, and dipole–quadrupole interaction energies. In section III, we introduce the WKB wave functions to calculate the collision integral. The collision integral will be calculated indirectly from that for the Morse potential alone and that for the LJ-dipole–quadrupole interaction energy. In section IV, we average the terms in the collision integral representing the charge interaction over the rotation of the dipoles. It is important to emphasize here that calculated values of $P(T)$ shown in section V are not reliable because of uncertainties in the formulation of the

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

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[10] K. Takayanagi, *Sci. Rept. Saitama Univ.*, A3, 1 (1958).

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[17] P. G. Corran, J. D. Lambert, R. Salter, and B. Warburton, *ibid.*, S244, 212 (1958).

[18] F. D. Shields, *J. Chem. Phys.*, 46, 1063 (1967).

perturbation energy shown in section II. However, these uncertainties affect only the weakly temperature-dependent preexponential factor of $P(T)$. Therefore, the numerical analysis *correctly* represents the temperature dependence of intermolecular energy transfer which is the prime objective of the present investigation.

II. Interaction Energy

In any quantum mechanical theory of inelastic molecular-scattering processes, the transition probabilities or cross sections are found to depend on the matrix elements of the interaction energy. If x represents the displacement of the oscillator from its equilibrium position, the interaction, in the case of interest here, may be assumed linear in the internal displacement

$$V(r,x,\text{ angles}) = U(r,0,\text{ angles}) - xF(r,\text{ angles}) \quad (4)$$

This expression may also be considered as the leading part of the expansion of V about x obtained neglecting higher order terms, and thereby assuming that the amplitude of vibration is small compared to the range of the potential. Such expansion can be a satisfactory procedure if V is a function of $r - x$. The function F is the perturbing force, which is in general difficult to give in an explicit form for polyatomic molecules. If V were a function of $r - x$ alone at given molecular orientations, then F would be simply U'. The force which determines the relative translational motion, $-U'$, does not consist only of $-F$, but also of an additional force which would act between the colliding molecules even if no force acted on the oscillator itself. As shown in section III, however, while not much is known about F, its effects appear only in the preexponential part of the transition probability. Since the temperature dependence of intermolecular energy transfer is dominated by the exponential part of $P(T)$, to which the present discussion is restricted, the detailed nature of F is relatively unimportant here. Furthermore, the matrix element of x introduced in eq 4, or of other forms which may be assumed, is independent of initial energies (or temperature, if an average over a Boltzmann distribution is performed). In eq 4, the function $U(r,0,$ angles) is a typical angle-dependent (unperturbed) interaction energy, determining the relative translational motion of the molecules.

The intermolecular potential model adopted is the Morse potential with added dipole–dipole and dipole–quadrupole interaction terms

$$U = U(r,0,\text{ angles}) = D[\exp(-r/a) - 2\exp(-r/2a)] - (\mu^2/r^3)g - (3\mu Q/2r^4)h \quad (5)$$

where μ and Q are dipole and quadrupole moments, respectively, and g and h are the orientation dependent factors[19]

$$g(\Gamma_1,\Gamma_2,\omega) = 2\cos\Gamma_1\cos\Gamma_2 - \sin\Gamma_1\sin\Gamma_2\cos\omega \quad (6\text{-}1)$$

$$h(\Gamma_1,\Gamma_2,\omega) = {}^1\!/_2(\cos\Gamma_1 - \cos\Gamma_2) \times (2\sin\Gamma_1\sin\Gamma_2\cos\omega - 3\cos\Gamma_1\cos\Gamma_2 - 1) \quad (6\text{-}2)$$

where $\omega = \omega_2 - \omega_1$ and the angles are defined in Figure 1. The above expressions (eq 6) are correct for molecules with axially symmetric charge distribution. In the calculation of $P(T)$ the change of these factors with orientation must be carefully considered, for it is only the Boltzmann principle that, by favoring positions of low energy, prevents these terms from vanishing when summed over all angles. Equation 5 is composed of four parts. All parts may be dependent on the relative orientation of the two molecules as well as on their distance apart, but such orientation dependence may be neglected for those forces which only fluctuate in magnitude but never change sign, *i.e.*, the first two terms. Thus, the main part of the interaction energy which is the Morse function is a spherically symmetric potential, so that usual perturbation schemes for the calculation of $P(T)$ for such potential may be used here. As we shall see below (section IV), the collision integral can be solved as a product of the angle-independent part (*i.e.*, from the Morse potential) and the angle-dependent part (*i.e.*, from the 3-4 inverse potential). The rotation of the axes of the dipoles represented in Figure 1 will affect only the latter part.

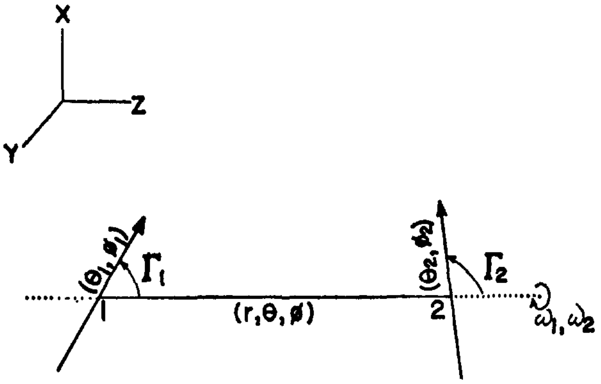

Figure 1. Points 1 and 2 represent the centers of two molecules 1 and 2. The solid line through 1 indicates the axis of the dipole and the cylindrically symmetric quadrupole of molecule 1, and the line through 2 indicates the similar axis for the second molecule. The intermolecular distance is r, and the angles Γ_1, Γ_2, ω_1, and ω_2 serve to define the orientations of the two axes. θ_1, ϕ_1, θ_2, and ϕ_2 describe the direction of the axes.

Rowlinson[20,21] assumed the 12-6-3-4 inverse potential for the calculation of the second virial coefficient of water vapor

$$U = 4D[(\sigma/r)^{12} - (\sigma/r)^6 - (\sigma/r)^3t^*g - (\sigma/r)^4u^*h] \quad (7)$$

where $t^* = \mu^2/4D\sigma^3$, $\mu^* = 3\mu Q/8D\sigma^4$, and σ is $U(\sigma) = 0$ that would apply in the zero dipole and quadrupole limits. Inverse power laws have been favorite representation of the molecular interactions partly because the evaluation of their collision integrals is relatively simple. However, it often happens that an exponential function gives a better representation of the interaction than does an inverse power at small intermolecular separations, but the evaluation of the collision integrals for an exponential interaction requires special mathematical techniques since now the over-all interaction energy is a sum of the exponential and inverse power (3-4) laws.

For very high collision energies, where the repulsive forces are more important than the attractive forces, it

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[19] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1964, pp 27, 35, 225–226.

[20] J. S. Rowlinson, *Trans. Faraday Soc.*, **47**, 120 (1951).

[21] Also see, N. Bjerrum, *Kgl. Danske Videnskab. Selskab Mat. Fys. Medd.*, **27**, 1 (1951); *Science*, **115**, 385 (1952).

is a fairly good approximation to replace the angle-dependent interaction by the expression which corresponds to the interaction of two-point dipoles (in the dipole–dipole interaction) which are perfectly aligned. This allows us to write the Krieger potential by neglecting the dipole–quadrupole interaction. Although molecular quadrupole moments are normally about 10^{10} times nuclear moments, they are not easy to measure directly owing to our inability to produce sufficiently large macroscopic field gradients. Interaction energies of about 10^{-23} erg can be obtained, while for dipoles in fields of 10 esu the energy is about 10^{-17} erg. At a point of a few angstrom units from a polar molecule, the field gradient is about 10^{14} esu, whereas the field is about 10^{6} esu. Thus molecular quadrupoles will contribute significantly to intermolecular forces.

III. Vibrational Transition Probability

Because of the complicated angle and distance dependences of the terms in eq 5, the calculation of vibrational transition probabilities and related quantities is excessively difficult. In earlier investigations,[13,14] such calculations have been attempted for the Krieger potential. However, for any inelastic collision such averaging prior to the calculation of the collision integral is unrealistic or perhaps it is totally unacceptable for polar molecules. The colliding molecules may transfer their energies more easily when they interact with a "particular orientation." For example, it is thought that the longitudinal vibration of a linear molecule is most efficiently excited or deexcited when the velocity of relative motion is along its axis (*i.e.*, a colinear collision). For nonlinear molecules, say triatomic molecules, the bending vibration can be effectively excited or deexcited when the two (identical) molecules are approaching parallel to each other. There are also preferred orientations of the permanent charges as pointed out above; if such orientations are favorable for the energy transfer, the transition probability can be very large at this particular angle or angles. When we average the interaction energy before the calculation of the collision integral, it would mean that we weighted all orientations equally for the energy transfer and no emphasis to particular orientations is given; perhaps this is a satisfactory treatment for completely spherical molecules or for collisions at high temperatures. For polar molecules particularly at low temperatures in which the permanent charges tend to be distributed along particular directions, we must consider the importance of the angle dependence of the vibrational transition probability. Therefore, the vibrational transition probability per collision (or per second) should be formulated as a function of the initial relative energy E and the orientation of the molecular symmetry axes or the direction of the dipoles, $P(E$, angles). The thermal average transition probability should still be a function of the angles, $P(T$, angles), for such cases. Finally, we must average $P(T$, angles) over all possible rotations of the dipoles to obtain $P(T)$. If we started with the calculation of $P(T)$ with an angle-dependent Morse potential, $P(E$, angles) is a function of both the angles of molecular rotations and the rotations of the axes of the permanent charges, which are not identical with each other unless the molecules are linear. For this type of potential the calculation is considerably difficult (but not impossible).

At low temperatures, molecules will not suffer a violent change in the vibrational motion during encounter. As to the rotational state, this statement may not be very accurate, but it will still be convenient to start with expanding the complete wave function of the collision system in terms of the free rotational and vibrational wave functions of molecules. Provided the duration of the encounter is longer than the period of molecular rotation and vibration, and provided the distortion is nearly adiabatic, the perturbed stationary state (PSS) method[4,22] can be used to treat the collision systems. Unless the energy of relative motion is high, this method is favored over others such as the distorted wave (DW) method[4,22] for treating rotational transitions in collisions between strongly polar molecules and vibrational transitions of a molecule with a relatively small force constant. The probability $P(E$, angles), where the angles resulted only from the interaction between the permanent charges on the colliding molecules, that the molecule (or oscillator) will undergo the transition from internal state $\phi(x)$ to $\phi'(x)$, while the incident molecules' relative motion changes from an energy state E to E' $(=E+\Delta)$ due to the transition, may be calculated by the DW method. Alternatively, it may be calculated by the PSS method with the assumptions that the perturbation of the oscillator energy levels and wave functions by $-xF(r)$ is adequately given by first-order perturbation theory. Note that, as will be discussed below, we essentially use here the perturbation energy $-xF(r)$ rather than $-xF(r$, angles) in the calculation of the transition probability. In either the PSS or DW methods, it follows from eq 4 that the probability of intermolecular energy transfer per collision is given by the following formula[8,23]

$$P(E,\ \text{angles};j) = \frac{8m}{\hbar^2\sqrt{E(E+\Delta)}}\left|\int_0^\infty\int_{-\infty}^\infty \mathcal{R}_j'(r,E+\Delta)\phi'(x)[V(r,x,\ \text{angles})]\phi(x)\mathcal{R}_j(r,E)\,\mathrm{d}x\mathrm{d}r\right|^2 = \frac{8m}{\hbar^2\sqrt{E(E+\Delta)}}[\beta_j(E,\ \text{angles})]^2 \quad (8)$$

where the second relation defines the collision integral $\beta_j(E$, angles). The wave function $\mathcal{R}_j(r,E)$ is the well-behaved solution of

$$\left[\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}r^2} + E - U - \frac{\hbar^2 j(j+1)}{2mr^2}\right]\mathcal{R}_j(r,E) = 0 \quad (9)$$

which is normalized so that as $r \to \infty$.

$$\mathcal{R}_j(r,E) \sim \cos\left(\frac{\sqrt{2mE}}{\hbar}r + \delta\right) \quad (10)$$

and $\mathcal{R}_j(0,E) = 0$, where δ may depend on E and on j but is independent of r. The oscillator wave function $\phi(x)$ may be assumed by either the harmonic or Morse oscillator wave functions. In the above formulation we neglected the transfer of rotational energy compared to that of vibrational energy. Every collision will then be characterized by the quantum number j of the rela-

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

(23) C. Zener, *Phys. Rev.*, 37, 556 (1931).

tive angular momentum, which has the same value both during the approach and recession of the colliding molecules.

As noted in the formulation of the interaction energy above, the angle dependence of the collision integral is caused by the interaction between the permanent charges, and we now must average this dependence over all possible rotations of the coordinate. For this purpose we introduce the rotational functions containing spherical harmonics

$$Y_i = \frac{1}{\sqrt{2\pi N_{l_i}^{(m_i)}}} P_{l_i}^{(m_i)} \exp(-im_i\phi_i)$$

for the rotation of the ith dipole, and $S_j = (2\pi N_j)^{-1/2}P_j$, for the relative motion, where P's are the Lengendre functions and N's are the normalizing constants. The angles θ_i and ϕ_i are for the directions of the charge axes shown in Figure 1, and r, θ, and ϕ are the spherical coordinate of the radius vector from the center 1 to 2 also shown in Figure 1. Therefore, the orientation-averaged expression of the vibrational transition probability can be formulated by

$$P(E) = \frac{8m}{\hbar^2\sqrt{E(E+\Delta)}}\iiint Y_1^*Y_2^*S_j^* \times [\beta_j(E, \text{angles})]^2 S_jY_2Y_1\, d\Omega d\Omega_2 d\Omega_1 \quad (11)$$

where $d\Omega$, $d\Omega_1$, and $d\Omega_2$ are the elements of solid angles for relative motion and the orientation of the axes: $\sin\theta\, d\theta d\phi$, $\sin\theta_1\, d\theta_1 d\phi_1$, and $\sin\theta_2\, d\theta_2 d\phi_2$.

It should be noted that we could have averaged $P(E,$ angles; $j)$ simply over the elements of solid angles without the consideration of the rotational functions Y's. However, we believe that the above procedure is physically preferred since eq 11 is a quite general form. For example, if we express the transition probability as

$$P(E) = \frac{8m}{\hbar^2\sqrt{E(E+\Delta)}}\iiint Y_1'^*Y_2'^*S_j'^* \times [\beta_{jj'}(E, \text{angles})]S_jY_2Y_1\, d\Omega d\Omega_2 d\Omega_1{}^{2} \quad (12)$$

we could determine the effect of rotational transitions on the vibrational energy transfer, where the primed functions and j' designate the values after the transition. If we neglect the transfer of rotational energy compared to that of vibrational energy and sum over all possible final states, j', l_1', and l_2', keeping a fixed initial state, j, l_1, l_2, we may write this expression as[24]

$$P(E) = \frac{8m}{\hbar^2\sqrt{E(E+\Delta)}}\iiint Y_1^*Y_2^*S_j^* \times [\beta_j(E, \text{angles})]^2 S_jY_2Y_1\, d\Omega d\Omega_2 d\Omega_1 \quad (13)$$

which is identical with eq 11.

Assuming a Boltzmann distribution of the initial energies we define the (thermal) average transition probability at any temperature as

$$P(T) = \int_0^\infty P(E)(E/kT)\exp(-E/kT)\, d(E/kT) \quad (14)$$

By substituting eq 11 into eq 14, we obtain

$$P(T) = \frac{8m}{(\hbar kT)^2}\iiint Y_1^*Y_2^*S_j^*\left\{\int_0^\infty \sqrt{\frac{E}{E+\Delta}} \times \exp(-E/kT)[\beta_j(E, \text{angles})]^2\, dE\right\} S_jY_2Y_1\, d\Omega d\Omega_2 d\Omega_1 \quad (15)$$

Now, let us evaluate the collision integral, which takes the following form for the interaction energy given by eq 4

$$\beta_j(E, \text{angles}) = \mathbf{x}\int_0^\infty \mathcal{R}_j'(r,E+\Delta)F(r, \text{angles})\mathcal{R}_j(r,E)\, dr \quad (16)$$

where the matrix element is $\mathbf{x} = \int_{-\infty}^{\infty}\phi'(x)x\,\phi(x)\, dx$. In the region of strong interaction the attractive part of F inserted in eq 16 is insignificant compared to the repulsive part. Of course, the effect of the attractive forces acting between the colliding molecules is important in determining the probability of intermolecular energy transfer, but the effect is essentially controlled by the attractive terms in the exponent of the wave functions which contains the unperturbed interaction energy U.[25] The wave functions always vary much more rapidly compared to the perturbing force itself at small r, and the effect due to the attractive forces in the wave functions directly enters in the exponent of the transition probability, whereas the effect in F enters in the preexponential part which is weakly energy or temperature dependent. Therefore, we neglect the attractive part in F in eq 16 but not that in the wave functions; *i.e.*, the perturbing force is then independent of the angles. The angle-dependent force could have been obtained if we assumed an angle-dependent repulsive term in eq 5.

We assume the wave functions by the following WKB forms[26–28]

$$\mathcal{R}_j(r,E) = \frac{c}{[2m(U_e - E)]^{1/4}} \times \exp\left[\hbar^{-1}\int_{r_0}^{r}\sqrt{2m(U_e - E)}\, dr\right] \quad (17\text{-}1)$$

$$\mathcal{R}_j'(r,E') = \frac{c'}{[2m(U_e - E')]^{1/4}} \times \exp\left[-\hbar^{-1}\int_{r'_0}^{r}\sqrt{2m(U_e - E')}\, dr\right] \quad (17\text{-}2)$$

where $c = (2\pi mE/8)^{1/4}$, $c' = (2\pi mE'/8)^{1/4}$, and r_0 is the largest root of $(U_e - E) = 0$. The effective potential is

$$U_e = U(r,0,\text{ angles}) + \frac{\hbar^2 j(j+1)}{2mr^2} \quad (18)$$

The evaluation of the r integral given in eq 16 for the effective potential

$$U_e = 4D[(\sigma/r)^{12} - (\sigma/r)^6] + \frac{\hbar^2 j(j+1)}{2mr^2} \quad (19)$$

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[24] Reference 2, pp 295–296, 305–307.

[25] H. Shin, *J. Chem. Phys.*, **47**, 3302 (1967).

[26] L. Landau and E. M. Lifshitz, "Quantum Mechanics," Pergamon Press, Inc., London, 1958, pp 178–183.

[27] B. Widom, *Discussions Faraday Soc.*, **33**, 37 (1962).

[28] H. Shin, *J. Chem. Phys.*, **46**, 744 (1967).

has been shown in ref 28. The same procedure cannot be employed here because the interaction energy is now a mixture of the exponential and inverse-power terms. An indirect way of solving the r integral for such a potential function is to evaluate the r integral for the 12-6-3-4 function followed by the replacement of the terms resulted from the LJ potential by those of the Morse potential. This matching procedure yields an expression for the exponential range parameter a in terms of the LJ potential parameters:[8] $a = (\sigma/\sqrt{\pi})\cdot[\Gamma(^7/_{12})/\Gamma(^1/_{12})](4D/E)^{1/12}$. By substituting the wave functions into eq 16 and using the Eulerian integral of the first kind,[29] the r integral is found as follows

$$\beta_j(E, \text{angles}) = \pi\sqrt{\frac{\hbar}{\Delta}}\left[\frac{E(E+\Delta)}{2m}\right]^{1/4}\left[\frac{U^{*1/4}F^*}{|U'^*|^{1/2}}\right]\mathrm{x} \times$$
$$\exp\left[\hbar^{-1}\sqrt{\frac{\pi m}{2}}\sum_{i=0}^{\infty}\sum_{n=1}^{\infty}\frac{a_i(-1)^n\Delta^n}{n!}\frac{\Gamma(n+i-{}^5/_{12})}{\Gamma(i+{}^{13}/_{12})}E^{5/12-n-i}\right] \tag{20}$$

$$n = 1, 2, 3, \ldots;\ i = 0, {}^1/_2, {}^2/_3, {}^3/_4, {}^5/_6, 1, \ldots$$

and

$$a_0 = (4D)^{1/12}\sigma/12$$
$$a_{1/2} = -7a_0\sqrt{D}/6$$
$$a_{2/3} = -3(4D)^{2/3}a_0u^*h/4$$
$$a^{3/4} = -5(4D)^{3/4}a_0t^*g/6$$
$$a_{5/6} = \frac{11}{24}\frac{\hbar^2j(j+1)a_0}{m\sigma^2(4D)^{1/6}}$$
$$a_1 = 13a_0D/72, \ldots$$

where U^*, U'^*, and F^* are the functions evaluated at $r = r^*$.

For the 12-6-3-4 function, the leading part of the collision integral is $\exp(-\text{constant}/E^{7/12})$, whereas the Boltzmann factor is $\exp(-E/kT)$. Therefore, the exponential part of the E integral given in eq 15 will take a maximum value at $E = E^*$, which is the root of the first derivative of the exponent set equal to zero. After a tedious calculation, this energy which we shall call "the most probable energy for the transition" is found to be

$$E^* = \chi_{\mathrm{LJ}} + \frac{13}{931}\left(\frac{\Gamma(^1/_{12})}{\Gamma(^7/_{12})}\right)^2\left(\frac{a_{1/2}}{a_0}\right)\chi_{\mathrm{LJ}}^{1/2} + \frac{5}{399}\times$$
$$\frac{\Gamma(^1/_{12})\Gamma(^3/_{12})}{\Gamma(^7/_{12})\Gamma(^9/_{12})}\left(\frac{a_{2/3}}{a_0}\right)\chi_{\mathrm{LJ}}^{1/3} + \frac{32}{665}\frac{\Gamma(^1/_{12})\Gamma(^4/_{12})}{\Gamma(^7/_{12})\Gamma(^{10}/_{12})}\left(\frac{a_{3/4}}{a_0}\right)\times$$
$$\chi_{\mathrm{LJ}}^{1/4} + \frac{85}{1463}\frac{\Gamma(^1/_{12})\Gamma(^5/_{12})}{\Gamma(^7/_{12})\Gamma(^{11}/_{12})}\left(\frac{a_{5/6}}{a_0}\right)\chi_{\mathrm{LJ}}^{1/6} + \frac{1596}{1729}\frac{a_1}{a_0} -$$
$$\frac{1}{114}\left(\frac{13}{98}\right)^2\left(\frac{\Gamma(^1/_{12})}{\Gamma(^7/_{12})}\right)^4\left(\frac{a_{1/2}}{a_0}\right)^2 \tag{21}$$

where

$$\chi_{\mathrm{LJ}} = \left[\frac{\Gamma(^{19}/_{12})}{\Gamma(^1/_{12})}\frac{(4D)^{1/12}\sqrt{2\pi m}\sigma\Delta kT}{\hbar}\right]^{12/19}$$

The E integral can be evaluated at $E = E^*$ by using the Laplace method for integrals.[30] The result is

$$\int_0^\infty\sqrt{\frac{E}{E+\Delta}}\exp(-E/kT)[\beta_j(E, \text{angles})]^2\,\mathrm{d}E =$$
$$\left[\frac{\pi^2\hbar}{\Delta\sqrt{2m}}\frac{U^{*1/2}F^{*2}}{|U'^*|}\right]\mathbf{x}^2\sqrt{\frac{4\pi kT}{3}}E^{*3/2}\exp\left\{-\frac{19\chi_{\mathrm{LJ}}}{7kT} + \right.$$
$$\frac{1}{42}\left(\frac{\Gamma(^1/_{12})}{\Gamma(^7/_{12})}\right)^2\frac{\sqrt{D\chi_{\mathrm{LJ}}}}{kT} + \frac{1}{21\sqrt{2}}\left(\frac{\Gamma(^1/_{12})\Gamma(^4/_{12})}{\Gamma(^7/_{12})\Gamma(^{10}/_{12})}\right)\frac{\mu^2}{D\sigma^3}\times$$
$$\frac{D^{3/4}\chi_{\mathrm{LJ}}^{1/4}g}{kT} + \frac{3(4)^{2/3}}{448}\frac{\Gamma(^1/_{12})\Gamma(^3/_{12})}{\Gamma(^7/_{12})\Gamma(^9/_{12})}\left(\frac{\mu Q}{D\sigma^4}\right)\frac{D^{2/3}\chi_{\mathrm{LJ}}^{1/3}}{kT}h -$$
$$\frac{5}{168}\frac{\Gamma(^1/_{12})\Gamma(^5/_{12})}{\Gamma(^7/_{12})\Gamma(^{11}/_{12})}\left[\frac{\hbar^2j(j+1)}{m\sigma^2(4D)^{1/6}}\right]\frac{\chi_{\mathrm{LJ}}^{1/6}}{kT} +$$
$$\left.\frac{19}{2}\left(\frac{13}{1596}\right)^2\left(\frac{\Gamma(^1/_{12})}{\Gamma(^7/_{12})}\right)^4\frac{D}{kT} - \frac{D}{6kT} + \frac{\Delta}{2kT}\right\} \tag{22}$$

In the exponent of eq 22, the first, second, sixth, and seventh terms resulted from the LJ(12-6) function in U. When these terms are replaced by the corresponding terms of the Morse potential through the matching relation between σ and a, we obtain the result for the Morse 3-4 function. For the simple Morse potential the transition probability is, when we assume $U'^* = F^*$

$$P_0(E) = \left(\frac{4\pi ma\Delta}{\hbar^2}\right)^2\mathbf{x}^2\times$$
$$\exp\left[\frac{\sqrt{2\pi m}}{\hbar}\sum_{i=0}^{\infty}\sum_{n=1}^{\infty}\frac{a_i(-1)^n\Delta^n}{n!}\frac{\Gamma(n+i-{}^1/_2)}{\Gamma(i+1)}E^{1/2-n-i}\right] \tag{23}$$

where the coefficients are $a_0 = a$, $a_{1/2} = -a\sqrt{D}$, $a_1 = 0$, $a_{3/2} = aD^{3/2}/2$, ... The temperature average of this expression results in

$$P_0(T) = \sqrt{\frac{4\pi}{3}}\left(\frac{4\pi ma\Delta}{\hbar^2}\right)^2\mathbf{x}^2\left(\frac{\chi}{kT}\right)^{3/2}\times$$
$$\exp\left[-\frac{3\chi}{kT} + \frac{4\sqrt{D\chi}}{\pi kT} + \frac{16D}{3\pi^2kT} + \frac{\Delta}{2kT}\right] \tag{24}$$

This equation is then based on the assumption of a spherically symmetrical field and might therefore be expected to apply to polar gases only at higher temperatures, where the molecules are in rapid rotation.

Before we write down the result for the Morse-3-4 function, we now explicitly consider the role of the rotation of the dipoles. The fifth term in the exponent of eq 22 represents the effect of the centrifugal quasi-potential energy. This term may be written

$$\left[\frac{5}{84}\frac{\Gamma(^1/_{12})\Gamma(^5/_{12})}{\Gamma(^7/_{12})\Gamma(^{11}/_{12})}\left(\frac{r^*}{\sigma}\right)^2\right]\frac{\hbar^2j(j+1)}{2mr^{*2}kT}$$

where r^* is "the most probable distance for the energy transfer" for the inverse-power potential

$$r^* = \left(\frac{14\hbar\sigma^6}{\Delta}\sqrt{\frac{2D}{m}}\right)^{1/7}[1 + O(\hbar)]$$

The factor in the square brackets of the term is not significantly different from unity; we therefore write the exponential containing this term with good approximation

$$\exp\left[-\frac{\hbar^2j(j+1)}{2mr^{*2}kT}\right] = \exp[-\rho j(j+1)]$$

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(29) E. T. Whittaker and G. N. Watson, "Modern Analysis," University Press, Cambridge, England, 1962, Chapter 12.

(30) N. G. de Bruijn, "Asymptotic Methods in Analysis," North-Holland Publishing Co., Amsterdam, 1961, Chapter 4.

The average transition probability for the Morse-3-4 interaction energy may then be expressed by eq 25,

$$P(T) = \sqrt{\frac{4\pi}{3}}\left(\frac{4\pi ma\Delta}{\hbar^2}\right)^2 \mathbf{x}^2\left(\frac{\chi}{kT}\right)^{3/2} \exp\left[-\frac{3\chi}{kT} + \frac{4\sqrt{D\chi}}{\pi kT} + \frac{16D}{3\pi^2 kT} + \frac{\Delta}{2kT}\right] \times \sum_j (2j+1)\,\rho\,\exp[-\rho j(j+1)] \times \iiint Y_1^* Y_2^* S_j^* \exp\left\{\left[\frac{1}{21\sqrt{2}}\left(\frac{21}{19}\right)^{1/4}\frac{\Gamma(1/12)\Gamma(4/12)}{\Gamma(7/12)\Gamma(10/12)}\right] \times \left(\frac{\mu^2}{D\sigma^3}\right)\left(\frac{D^{3/4}\chi^{1/4}}{kT}\right)g + \left[\frac{3(4)^{2/3}}{448}\left(\frac{21}{19}\right)^{1/3}\frac{\Gamma(1/12)\Gamma(3/12)}{\Gamma(7/12)\Gamma(9/12)}\right] \times \left(\frac{\mu Q}{D\sigma^4}\right)\left(\frac{D^{2/3}\chi^{1/3}}{kT}\right)h\right\} S_j Y_2 Y_1 \,\mathrm{d}\Omega\mathrm{d}\Omega_2\mathrm{d}\Omega_1 \quad (25)$$

where the contribution of a term with $S_j = (2\pi N_j)^{-1/2}P_j$ has been weighted by the factor[24] $(2j + 1)\rho \exp[-\rho j\cdot(j + 1)]$. The first term in the last exponent is due to the dipole–dipole interaction and the second the dipole–quadrupole interaction, both still being functions of the orientation angles Γ_1, Γ_2, ω_1, and ω_2. Equation 25 may be written in the following alternative form

$$P(T) = \sum_j (2j + 1)\rho \exp[-\rho j(j + 1)] \times \iiint Y_1^* Y_2^* S_j^* [P(T,\ \text{angles})] S_j Y_2 Y_1 \,\mathrm{d}\Omega\mathrm{d}\Omega_2\mathrm{d}\Omega_1 \quad (25\text{a})$$

IV. Average Over Angles

The probability of a state l_i, m_i of the axis of the dipole and the symmetric quadrupole of the ith molecule is given by[24] $\rho_i \exp[-\rho_i l_i(l_i + 1)]$, where $i = 1, 2$ and $\rho_i = \hbar^2/2I_ikT$, I_i being the moment of inertia. Therefore, the angle-averaged form is

$$P(T) = P_0(T)\iint \sum_j [(2j + 1)\rho \exp[-\rho j(j + 1)] \times \frac{P_j^2}{2\pi N_j} \sin\theta \ \mathrm{d}\theta\mathrm{d}\alpha \iiiint \sum_{l_1}\sum_{l_2} \rho_1\rho_2 \exp[-\rho_1 l_1(l_1 + 1) - \rho_2 l_2(l_2 + 1] \sum_{m_1}\sum_{m_2} \frac{(P_{l_1}^{m_1})^2}{2\pi N_{l_1}^{m_1}} \frac{(P_{l_2}^{m_2})^2}{2\pi N_{l_2}^{m_2}} \times \exp(\alpha g + \beta h) \sin\theta_1 \,\mathrm{d}\theta_1\mathrm{d}\phi_1 \sin\theta_2 \,\mathrm{d}\theta_2\mathrm{d}\phi_2 \quad (26)$$

where α and β are the coefficients of g and h given in eq 25, respectively. This is a formal expression for the case of the collision between two diatomic molecules. For symmetric top molecules, the weighting factor should contain two parts, one representing the l dependence and the other the K dependence, where $K = 0, \pm 1, \pm 2, \ldots, \pm l$, so that the factor is $\rho_i\rho_i' \exp[-\rho_i l_i(l_i + 1) - \rho_i' K_i^2]$, for the ith molecule, where $\rho_i' = (1/I_A - 1/I_B)\hbar^2/2kT$ and ρ now contains I_B with $I_C = I_B > I_A$. When ρ_i' is small compared to unity, we can replace, with good approximation, the K_i sum by an integral to obtain unity; then the result is identical with eq 26. The evaluation of eq 26 can be greatly simplified if we use Unsöld's theorem, which states that the sum of all the probability distribution for a given l is a constant[31]

$$\sum_{m=-l}^{+l} \frac{(P_l^m)^2}{2\pi N_l^m} = \frac{2l + 1}{4\pi}$$

When ρ_1 and ρ_2 are small compared to unity, we can replace the l sums by integrals, and obtain $^1/_2$ for each. Equation 26 then becomes

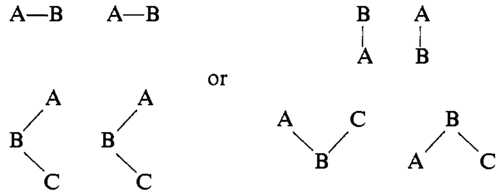
$$P(T) = P_0(T)\left\{\frac{1}{4}\iint \sum_j (2j + 1)\rho \exp[-\rho j(j + 1)] \times \frac{P_j^2}{2\pi N_j} \sin\theta \ \mathrm{d}\theta\mathrm{d}\phi \iiiint \exp(\alpha g + \beta h) \times \sin\theta_1 \,\mathrm{d}\theta_1 \frac{\mathrm{d}\phi_1}{2\pi} \sin\theta_2 \,\mathrm{d}\theta_2 \frac{\mathrm{d}\phi_2}{2\pi}\right\} \quad (27)$$

The integration of the angle-dependent part is an excessively difficult task, if not impossible. It can be explicitly evaluated only when certain "physical" relations are assumed. To carry out the integrations, we simplify the functions g and h in the exponent of eq 26 as follows. The inclination angles are related with the directions of the coordinates as

$$\cos\Gamma_1 = \cos\theta\cos\theta_1 + \sin\theta\sin\theta_1\cos(\phi_1 - \phi) \quad (28\text{-}1)$$

$$\cos\Gamma_2 = \cos\theta\cos\theta_2 + \sin\theta\sin\theta_2\cos(\phi_2 - \phi) \quad (28\text{-}2)$$

The maximum value of g is $+2$ for $\Gamma_1 = \Gamma_2 = 0$ or $\Gamma_1 = \Gamma_2 = \pi$; the minimum value is -2 for $\Gamma_1 = 0$, $\Gamma_2 = \pi$ or $\Gamma_1 = \pi$, $\Gamma_2 = 0$. The maximum value of h is also $+2$ but it appears at $\Gamma_1 = 0$, $\Gamma_2 = \pi$, and the minimum value, which is -2, occurs at $\Gamma_1 = \pi$, $\Gamma_2 = 0$. For linear molecules the colinear alignment is most effective in transferring the energy associated with the longitudinal motion. Even for nonlinear molecules, it is likely that the energies can exchange more efficiently when the colliding molecules' relative orientations are not very much "out of phase." From the favorable orientations of dipoles and quadrupoles the following alignments can be most effective for the energy transfer



The dipole direction will be →→ in the first case and ⇅ in the second (*i.e.*, the colinear and parallel collisions are most effective). Then, for an excitation of the lowest vibrational motion, the term $\sin\Gamma_1 \sin\Gamma_2 \cos\omega$ in both h and g can be neglected compared to the others in the first approximation. We introduce $\theta_1 = \theta + \delta_1$, $\theta_2 = \theta + \delta_2$, and $\phi_1' = \phi_1 - \phi$, $\phi_2' = \phi_2 - \phi$ in eq 28, δ_i and ϕ_i' being small quantities of the first order. With these substitutions and with the use of trigonometric identities we can approximate $\cos\Gamma_1 \simeq 1 - {}^1/_2\cdot(\delta_1^2 + \phi_1'^2\sin^2\theta)$ and $\cos\Gamma_2 \simeq 1 - {}^1/_2(\delta_2^2 + \phi_2'^2\sin^2\theta)$.

The function g can therefore be approximated in the form 1 − (angle-dependent terms). On the other hand, for h the factor $(\cos\Gamma_1 - \cos\Gamma_2)$ is small, the leading term being dependent on the angles. Thus h contains only terms dependent on the angles; *i.e.*, the leading term is a function of the angles. With these simplifications the angle-dependent part $\exp(\alpha g + \beta h)$ can be readily evaluated by extending the integrals from $-\infty$

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(31) A. Unsöld, *Ann. Phys.*, [4] 82, 355 (1927).

to $+\infty$ because of the steepness of the exponential parts containing δ_i and ϕ_i'.

$$\exp(2\alpha)\iiiint_{-\infty}^{\infty}\exp\{-\alpha(\delta_1{}^2 + \phi_1'^2 \sin^2\theta) - \alpha(\delta_2{}^2 + \phi_2'^2 \sin^2\theta) + \beta[\delta_1{}^2 - \delta_2{}^2 + (\phi_1'^2 - \phi_2'^2)\sin^2\theta]\}\sin^2\theta \, d\delta_1 d\delta_2 \frac{d\phi_1'}{2\pi}\frac{d\phi_2'}{2\pi} = \frac{\exp(2\alpha)}{4(\alpha^2 - \beta^2)} \quad (29)$$

Equation 27 is then

$$P(T) = P_0(T)\left[\frac{\exp(2\alpha)}{16(\alpha^2 - \beta^2)}\right]\iint\sum(2j + 1)\rho \times \exp[-\rho j(j + 1)]\frac{P_j{}^2}{2\pi N_j}\sin\theta \, d\theta d\phi \quad (30)$$

When ρ is sufficiently small compared to unity, the j sum can be replaced by an integral.[28] Since the integrations over θ and ϕ result in unity, the j sum is simply unity. Hence, the final expression for the average vibrational transition probability for the present model is

$$P(T) = \frac{A}{16(\alpha^2 - \beta^2)}\left(\frac{\chi}{kT}\right)^{3/2}\exp\left[-\frac{3\chi}{kT} + \frac{4\sqrt{\chi D}}{\pi kT} + \frac{16D}{3\pi^2 kT} + \frac{\Delta}{2kT} + 2\alpha\right] \quad (31)$$

or

$$P(T) = fP_0(T) \quad (31a)$$

where

$$A = \sqrt{\frac{4\pi}{3}}\left(\frac{4\pi m a\Delta}{\hbar^2}\right)^2 \mathbf{x}^2 \qquad f = \frac{\exp(2\alpha)}{16(\alpha^2 - \beta^2)}$$

This is the average vibrational deexcitation transition probability per collision with the magnitude of the change in the molecule's vibrational energy Δ; if it is a one-quantum transition ($1 \rightarrow 0$), then $\Delta = h\nu$. To obtain the form of the exponential part appropriate to an excitation of the molecule rather than to a deexcitation, we have merely to replace $\Delta/2kT$ by $-\Delta/2kT$.

V. Discussion

In the second relation of eq 31 the factor $P_0(T)$, the transition probability calculated from the Morse potential, is an increasing function of temperature and it gives an adequate description of the energy transfer process, within the limits of our present knowledge of intermolecular forces, in nonpolar molecules. However, the contribution due to the interaction of the permanent charges on the colliding molecules (*i.e.*, the factor f) can either increase or decrease or even it can first decrease and then increase when temperature increases. If a molecule has large dipole moment but a small molecular "diameter" σ that would apply in the zero dipole and quadrupole limits, then $\exp(2\alpha)$ can be very large at low temperatures, whereas α^2 is only moderately large. On the other hand, $\alpha^2 - \beta^2$ can become small if the magnitude of α is comparable to β; therefore, f is very large in such case. As temperature increases, $\exp(2\alpha)$ rapidly becomes small so that f can decrease. When temperature becomes still high, both α and β can be small, *i.e.*, the difference between α^2 and β^2 is also small, so that f may now increase. From eq 31, at low temperatures, the part $P_0(T)$ then tends to raise the over-all magnitude of $P(T)$, whereas f tends to lower $P(T)$ as temperature increases. Thus, if the change of f with T is strong enough to oppose (numerically) the normal temperature dependence of $P_0(T)$, the average transition probability may decrease to a minimum value and then increase in a normal fashion as temperature increases. Physically, this kind of anomaly can result because of the oriented collisions at low temperatures. The colliding pairs may take preferentially a "particular" relative orientation when they come close to each other at low temperatures, and at this orientation the energy transfer may take place more efficiently than in other orientations. As temperature increases, it is difficult to maintain such orientation owing to the increased freedom in molecular motions; consequently the transition becomes less probable than at low temperatures. At still higher temperatures, however, the molecular orientation may become completely random. Then, the factor $\exp(-3\chi/kT)$ in eq 31, which rapidly increases with temperature, dominates all other factors in the exponential part; $P(T)$ now increases with temperature.

From the expression for α, which represents the dipole–dipole interaction, we see that the magnitudes of μ and σ control the variation of f. For very polar molecules with relativity small σ, α is in general large at low temperatures and the T dependence of $P(T)$ can be anomalous. For example, for H_2O σ is 2.65 Å and μ is 1.84 D, and for SO_2 $\sigma = 4.026$ Å and $\mu = 1.7$ D. For the former system we may predict that the calculation of eq 31 can show a minimum in the $P(T)$–T relation, whereas for the latter it is doubtful because σ is quite large as for most polyatomic molecules. Also, HCN and ClCN have large values of both μ and Q, and the anomalous temperature dependence of $P(T)$ for these gases may be predicted. For NH_3 the dipole moment is 1.44 D and σ is 2.60 Å; for CH_3Cl the corresponding values are 1.87 D and 4.15 Å. Therefore, if the application of eq 31 is made, the anomalous behavior may result for NH_3. For CH_3Cl there may not be the minimum value of $P(T)$ since σ is large; *i.e.*, α is not large enough to cause the variation of f with temperature to counteract numerically the variation of $P_0(T)$. Of course, these qualitative predictions may not be correct since the quadrupole moment can significantly alter f. For most of the molecules mentioned above, no reliable value of the quadrupole moment is available[32] at present, so that an "accurate" calculation of f and in turn $P(T)$ given by eq 31 is not possible.

There are experimental evidences for such temperature dependence of $P(T)$ in certain polar molecules. Lambert and his coworkers[16,17] have reported that the probability of vibrational transition of SO_2, CH_3Cl, CH_3Br, and CH_3F has a minimum as a function of temperature (but we note that in their report the existence of such minimum for CH_3Br and CH_3F is somewhat doubtful). They interpreted this anomalous behavior as due to increasing predominance of oriented collisions which are specially favorable for energy transfer between polar molecules at low temperatures.

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(32) A. D. Buckingham, *Quart. Rev.* (London), 13, 183 (1959).

Recently Shields[18] reported that in pure SO_2 the transition probability per second $ZP(T)$, where Z is the collision frequency and which in a single-relaxation time case is approximately equal to the reciprocal of the relaxation time, decreases between 298 and 400°K and then increases slightly between 400 and 500°K. It is also interesting to note that in the experimental work for CO_2-H_2O by Eucken and his coworkers,[33,34] and most recently by Lewis and Lee,[35] there is an increase in the probability of energy transfer with falling temperature. The transition probability was found to increase steadily as the temperature fell from 673 to 373°K, and then to decrease between 373 and 293°K, which is the reverse of the variation observed for SO_2 and the chloromethanes. This behavior has been explained by Widom and Bauer[36] in terms of chemical affinity between the interacting pairs.

For collision systems involving polar molecules any rigorous interpretation of the effect of the permanent charges using eq 31 can be made only when both the dipole and quadrupole moments are known. Most of the molecular quadrupoles so far "measured" have been determined indirectly by studying the interactions of molecules; however, the values deduced are uncertain, for they depend upon doubtful assumptions concerning the nature of the intermolecular force field. In making numerical computations of $P(T)$ additional deterrents have been uncertainties in the form of the perturbation energy and the evaluation of the matrix element $\mathbf{x}$ in the preexponential factor. Some problems involved in the perturbing energy and their effect on $P(T)$ has been discussed above. The evaluation of the matrix elements for polyatomic molecules is very difficult. If we use the harmonic oscillator wave functions the matrix element for the $1 \rightarrow 0$ transition is simply $\mathbf{x}_{10} = \hbar/(2M\Delta)^{1/2}$, where M is the reduced mass of the oscillator. With this expression the preexponential factor of eq 31 is

$$A\left(\frac{\chi}{kT}\right)^{3/2} = \sqrt{\frac{4\pi}{3}}\left[8\pi^2\left(\frac{\Delta}{M}\right)\left(\frac{ma}{\hbar}\right)^2\right]\left(\frac{\chi}{kT}\right)^{3/2} \quad (32)$$

However, the mass M for a polyatomic molecule is a function of the definition of the normal coordinate and it is in general very difficult to estimate.[3,37] Cottrell and Ream[38] showed a procedure which can be used to estimate M for polyatomic molecules.

As we have discussed above, eq 4 may be obtained by expanding $V(r,x,$ angles). For example, for the collision between a diatomic molecule AB and an incident particle C, the instantaneous separation between the collision pair in a colinear collision is $r - (m_A/m_A + m_B)x = r - \gamma x$, so that if the molecule is homonuclear we have $r - x/2$. Therefore, if we want to use eq 31 for this system, then we should multiply the preexponential factor by $^1/_4$. When $m_A \ll m_B$ and the incident particle is approaching the side of B, γ can be a very small factor. For polyatomic molecules, at the preferred orientations of the dipoles, the similar situation may apply when we assume $V(r - \gamma x,$ angles), where γ may now depend on the definition of the normal coordinate, and eq 31 should be multiplied by γ^2. However, all these uncertainties essentially do not affect the temperature dependence of $P(T)$. The only possible effect that can result from these uncertainties is the perturbing force which finally results in part in the factor $(\chi/kT)^{3/2}$ in the preexponential part. Therefore, throughout the following numerical illustration, the absolute magnitude of $P(T)$ is not *reliable*, but the temperature dependence is *correct* in the domain of applicability of eq 11, and our following discussion refers entirely to this aspect.

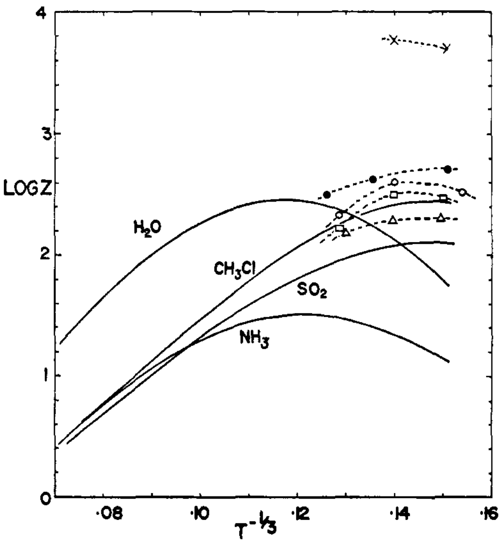

Figure 2. Plots of log Z_{10} *vs.* $T^{-1/3}$. Experimental data are: ×, CH_3F; ○, SO_2; □, CH_3Cl; △, CH_3Br from Lambert and Salter;[16] and ●, SO_2 from Shields.[18] (Note the ordinate represents log Z_{10}).

As discussed above, H_2O has a large μ and a small σ so that the exponential factor $\exp(2\alpha)$ can be very large at low temperatures. We first consider this system for numerical illustration. The quadrupole moment for this molecule is estimated as 2×10^{-26} esu. The lowest vibrational frequency is 1594.7 cm^{-1} and the depth of the potential well is taken to be $380k$. In Figure 2 the plot of log Z_{10} *vs.* $T^{-1/3}$ is made, where $Z_{10} = 1/P(T)$ for the $1 \rightarrow 0$ transition and is the number of collisions required to deexcite a quantum of vibrational energy. For this molecule a minimum value of log Z_{10} around 600°K is seen. No experimental data to substantiate this numerical result have been reported. Because of the important effect of the terms in the exponent of eq 31 resulting from the attractive energy and the term $\Delta/2kT$ which is large for "stiff" molecules, the variation of log Z_{10} with $T^{-1/3}$ is linear only above 1500°K. From 400 to 800°K log Z_{10} varies only slightly with temperature.

Since for SO_2 no reliable data on the quadrupole moment are available, we attempt to show the importance of the molecular orientations with $f' = \exp(2\alpha)/16\alpha^2$. The calculated values of log Z_{10} for $\nu = 519$ cm^{-1} are plotted in Figure 2 along with available experimental data. The chosen value of D is $363k$. Although we do not find the maximum value, the variation of log Z_{10} between 300 and 400° is very slight. Using the same factor f', we also calculate log Z_{10} for CH_3Cl-CH_3Cl with the values $\nu = 732$ cm^{-1}, $\mu = 1.87$ D, $\sigma = 3.94$ Å, and $D = 414k$. The variation of log Z_{10} with tem-

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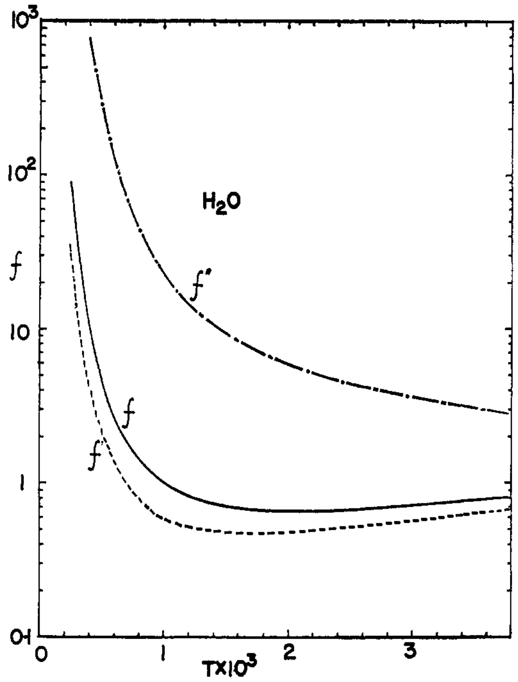

Figure 3. Plots of the factors f, f', and f'' for H_2O as a function of temperature.

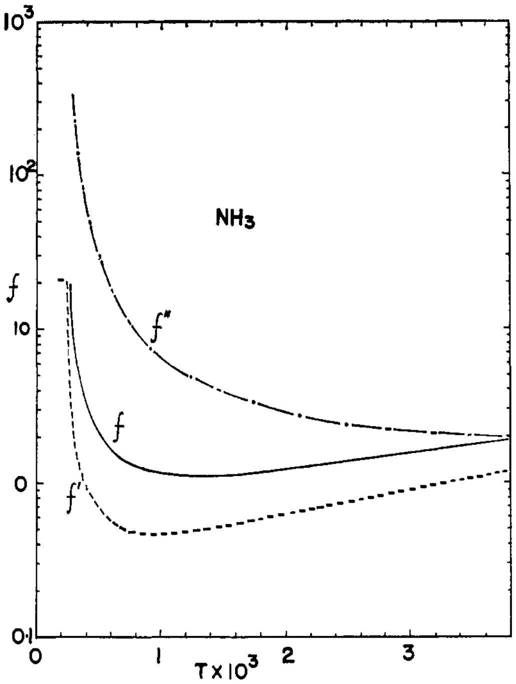

Figure 4. Plots of the factors f, f', f'' for NH_3 as a function of temperature.

perature is very similar to that for SO_2. No maximum value of the collision number is seen, but the change of log Z_{10} with temperature is very small between 300 and 400°K. Perhaps, the maximum may show up in the plot, if we introduce f rather than f' in the calculation.

For NH_3, the estimated value of Q is 1.3×10^{-26} esu; other constants are $\nu = 932.5$ cm^{-1} and $D = 320k$. Although the absolute value of log Z_{10} is significantly small, the variation is very similar to water molecules. A very slow change in log Z_{10} is seen between 400 and 800°K with the maximum value at about 500°K.

We show the variation of f with temperature in Figures 3 and 4 for H_2O and NH_3, respectively. The factor f varies very rapidly between 300 and 600°K and then reaches the minimum value at about 1400°K for H_2O and 900°K for NH_3. Around the minimum the T variation is not significant and it slowly increases as temperature increases. The importance of the dipole–quadrupole interaction can be seen by comparing f' with f. The difference between these two factors is about 2 for H_2O and about 4 for NH_3 at low temperatures. As temperature increases the difference becomes only slight, particularly for H_2O. It is interesting to show the variation of the factor $f'' = \exp(2\alpha)$ with temperature. This is the factor which will appear in $P(T)$ if we started the calculation of the transition probability with the Krieger potential. As shown in the two figures, this exponentially decreasing function of temperature is always very large compared to f and f'. Because of this continuously (and very rapidly) decreasing variation as temperature is increased, the factor $\exp(2\alpha)$ alone cannot numerically counteract the T variation of $P_0(T)$ in eq 31 to yield a maximum in the log Z_{10} *vs.* $T^{-1/3}$ plot, although it is possible that this factor alone can make the variation very slight at low temperature if μ is large and σ is small. From the difference between f and f'' or f' and f'', it is obvious that the Krieger potential always over-estimates the probability of intermolecular energy transfer in polar molecules over the temperature range considered here. This is not surprising since the calculation of $P(T)$ based on this potential implicitly assumes that all dipole orientations are equally effective in transferring energies between the vibrational and translational motions.

V. Concluding Remarks

The collisions systems which were chosen here to illustrate the temperature variation of $P(T)$ are by no means exhaustive. Equation 31 does, however, show the minimum in $P(T)$ at low temperatures for polar molecules with a small molecular "diameter" and large dipole and quadrupole moments, and it is clear that in the collision systems considered there must be a strong tendency for oriented collisions to take place between 300 and 600°K. Theories that have been developed so far are incapable of accounting for such anomalous temperature dependence of intermolecular energy transfer in polar molecules. If we assume spherically symmetric over-all interaction energies to calculate $P(T)$, it is not possible to show this type of anomaly. If we average the angle-dependent interaction energy between the permanent charges over all possible molecular orientations before calculating the collision integral, the resulting form of $P(T)$ will not also show such temperature dependence; rather the form will seriously over-estimate the probability. Therefore, we must carry along the angle dependence of the interaction energy throughout and obtain the transition probability as a function of the angles; finally, we must average the angle dependence over different dipole rotations to obtain $P(T)$.

We could have applied eq 31 to other systems to show the variation of $P(T)$ with T, but any rigorous calculation of the equation requires the values of Q which is not known for many molecules. The objective of the present investigation has been, however, to develop an expression which could be applied to explain the anomalous behavior in certain polar molecules.

Equilibria of Weak Complexes by Solution Calorimetry

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Abstract: Expressions are developed for determining thermodynamic parameters of several simple reaction mechanisms from the combination of two types of solution calorimetry experiments, heats of infinite dilution and heats of infinitesimal dilution. The advantages and limitations of combining these measurements are discussed. Application of the method is given for the cases of urea self-association and for purine self-association. In both cases it is shown that the thermodynamic quantities derived from the two types of heat measurements agree with those obtained from studies over a range of concentrations. The advantage of the procedure is the determination of weak interaction parameters on relatively dilute solutions.

The study of relatively weak hydrogen-bonding or charge-transfer complexes has relied mainly upon spectroscopic techniques.[2-4] Limited solubility or complications due to spectral absorption by the solvent can restrict their application. In those cases the methods of solution thermodynamics may be used.[2,4] The nonideal behavior, as measured by activity coefficients,[5,6] osmotic coefficients, or apparent molecular weights by sedimentation equilibria,[7] is interpreted in the context of various simple reactions. Under favorable circumstances, temperature derivatives of the evaluated free energies have been used to determine heats and entropies of reactions.

A less familiar approach has made use of mixing calorimetry.[8-10] In some cases sufficient information can be obtained to determine $\Delta G°$, $\Delta H°$, and $\Delta S°$ without auxiliary information; in other cases the combination of heats of dilution with osmotic coefficient data provides a route for $\Delta H°$ evaluations.[11]

In this paper we want to show how two types of solution calorimetry experiments, heats of infinite dilution and heats of infinitesimal dilution, can be used for the study of certain simple reactions involving weak interactions.

Heats of Infinite Dilution

When a solution containing m moles of solute and 1 kg of solvent is diluted by an infinite amount of solvent, the heat of this dilution is expressed by $-m\varphi_L$. The quantity φ_L is the relative apparent heat content. We assume this heat effect is due entirely to the dissociation of complex species into monomeric forms. Equilibria conditions govern the concentration of various species in the solution of molality m. For, example, self-association reactions might occur of the form with appropriate equilibrium constants and enthalpies of reaction

$$\begin{aligned} &\mathrm{A} + \mathrm{A} \rightleftarrows \mathrm{A_2} \qquad K_2,\ \Delta H_2° \\ &\mathrm{A} + \mathrm{A_2} \rightleftarrows \mathrm{A_3} \qquad K_3,\ \Delta H_3°,\ \text{etc.} \end{aligned} \tag{1}$$

In general, insufficient precision of measurements or incomplete validity of describing the nonideal behavior by such schemes precludes evaluation of more than one or two constants.

The heat of infinite dilution, $-m\varphi_L$, can be written formally in terms of molal concentrations as

$$m\varphi_L = (\mathrm{A_2})\Delta H_2° + (\mathrm{A_3})(\Delta H_2° + \Delta H_3°) + \cdots \tag{2}$$

or

$$m\varphi_L = K_2(\mathrm{A})^2\Delta H_2° + K_2K_3(\mathrm{A})^3(\Delta H_2° + \Delta H_3°) + \cdots$$

If all $\Delta H_n°$ values are equal to $\Delta H°$, then a simpler result[9-11] can be obtained with the definitions of the osmotic coefficient Φ

$$\varphi_L = (1 - \Phi)\Delta H° \tag{3}$$

This equation is applicable to any variety of reactions described by (1) for equal $\Delta H°$ values. Relative osmotic coefficients could be obtained by applying this equation in reverse.

If more restrictive conditions are imposed within eq 1, two special cases show similar concentration dependence of φ_L. For a dimerization reaction

$$\varphi_L = \frac{\Delta H_2°}{2} - {}^1\!/_2\left(\frac{\Delta H_2°}{K}\right)^{1/2}\left(\frac{\varphi_L}{m}\right)^{1/2} \tag{4}$$

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