CENTRIFUGAL EFFECTS IN REACTION RATE THEORY*

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Contents

I. Introduction

Early theories of unimolecular reaction rates have considered the role of overall molecular rotations by using two ostensibly different approaches; the results of both approaches are identical, however.

Eyring[1,2a] postulated that all degrees of freedom of the reactants are in thermodynamic equilibrium with those of the activated complex (except that special considerations attach to that degree of freedom associated with the reaction coordinate). In this simple formulation, and without specific considerat of the conservation of angular momentum, rotations contribute a factor to the high-pressure specific rate constant, k^∞_{uni}, for a unimolecular reaction which is the ratio of the square root of the moments of inertia of the rotational partition functions of the activated complex and the molecule, i.e., $(I_A^+ I_B^+ I_C^+ / I_A I_B I_C)^{1/2}$. Another approach that was applied even earlier to a diatomic approximation for unimolecular decomposition reactions is that of Rice and Gershinowitz (RG).[3] They pointed out that angular momentum conservation requires that the rotational quantum number does not change when the "activated complex" configuration at the top

of a potential barrier is reached from the excited molecule. If the product of the moments of inertia of the complex is larger than that of the molecule, then the centrifugal energy of the rotating molecule will effectively reduce the critical threshold vibrational energy and facilitate reaction. RG used a rigid rotor-activated complex with an (unspecified) fixed configuration. The averaged centrifugal effect enhances the rate constant by a factor which is again the square root of the moment of inertia ratio.

Marcus[4,5a] later gave a more detailed formulation of unimolecular reaction rates for the general pressure case in which the existence of centrifugal effects was formally mentioned in the context of the treatment of RG; however, the development did not lead to a correct formulation of the low-pressure limiting rate constant. Recently, Marcus[5c] modified the treatment to account explicitly for the effect of rotations on the microscopic rate constant, k_{EJ}, from which an appropriate form for the low-pressure limiting rate constant, k^0_{uni}, may be obtained; the high-pressure limiting expression was again recovered. The original theory of Eyring was not applied to the nonequilibrium unimolecular low-pressure region.

One matter regarding nomenclature may be mentioned. Marcus applied the term *adiabatic* to degrees of freedom characterized by a constant quantum number during the course of reaction in its mechanical sense. This has unequivocal significance for translational degrees of freedom and for rotations for which the moments of inertia remain constant throughout the course of reaction. The term is not used in its thermodynamic connotation; in the present application, rotational energy and vibrational energy are admixed and a total rotation–vibration potential expression is employed. However, the total number of relevant complexions of the system at the appropriate total energy of the active degrees of freedom are exclusively internal in nature. Since contributions of internal degrees of freedom to the total angular momentum, where relevant, are neglected, an overestimate of the vibrational–internal rotational density of states results in this treatment.

Centrifugal effects have also been included in the treatment of recombination reactions. Again, different approaches have led to agreement. The collision theory has been applied to the rate of bimolecular radical–radical[6,7] and ion–molecule[6,8] reactions; it is assumed that there is no activation energy for

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* Work supported by the National Science Foundation.

(1) H. Eyring, *J. Chem. Phys.*, 3, 107 (1935).

(2) S. Glasstone, K. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941: (a) pp 10–16; (b) p 220, 260; (c) p 213; (d) p 192.

(3) O. K. Rice and H. Gershinowitz, *J. Chem. Phys.*, 2, 853 (1934).

(4) R. A. Marcus and O. K. Rice, *J. Phys. Colloid Chem.*, 55, 894 (1951).

(5) (a) R. A. Marcus, *J. Chem. Phys.*, 20, 359 (1952); (b) G. M. Wieder and R. A. Marcus, *ibid.*, 37, 1835 (1962); (c) R. A. Marcus, *ibid.*, 43, 2658 (1965).

(6) K. Yang and T. Ree, *ibid.*, 35, 588 (1961).

(7) B. H. Mahan, *ibid.*, 32, 362 (1960).

(8) G. Gioumousis and D. P. Stevenson, *ibid.*, 29, 294 (1958).

the rotationless ($J = 0$) case in both reactions. The results of these treatments agree with the equilibrium theory treatments of Eyring and coworkers[2b,9,10] and of Gorin.[11,12]

Some misunderstanding and errors have developed in recent papers regarding the computation of appropriate averaged moments of inertia and the occurrence, treatment, and magnitude of the centrifugal effects. We present here an evaluation and summary of the use and applications that have been made of the theory thus far and demonstrate the utility of Marcus' expression for centrifugal effects[5c] in the general pressure region. Some average rotational energies are calculated for the activated complex and molecule, particularly the energy of the rotationally hot molecule formed from a bimolecular association.

II. Unimolecular Decomposition at High Pressure

A. CASE I. LARGE BARRIER FOR REVERSE ASSOCIATION REACTION

We summarize a treatment based on that of RG. An intermolecular potential of the form shown in Figure 1 is used.
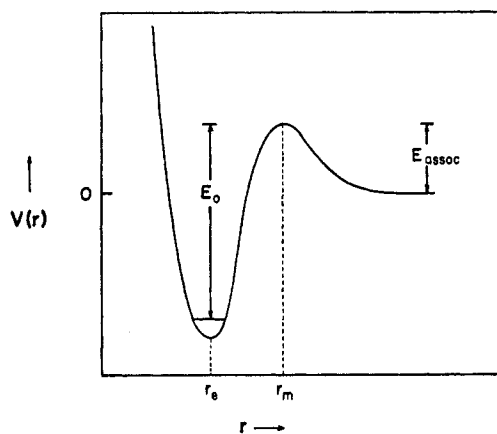

Figure 1. Case I potential energy diagram; the value of r_m is fixed for all rotational states.

Since one of the three moments of inertia tends to be invariant during reaction, the simplifying approximation is made that the molecule can be treated as a diatomic molecule, the two dissociating fragments being represented as mass centers. The energy of rotation is

$$E_J(r) = J(J + 1)\hbar^2/2\mu r^2 \tag{1}$$

where $J(J + 1)\hbar^2$ is the square of the total angular momentum, μ is the reduced mass, and r is the separation between the centers of mass. This rotational or centrifugal energy is added to the potential energy to obtain an effective potential V_{eff}, where

$$V_{eff}(r) = V(r) + E_J(r) \tag{2}$$

(9) H. Eyring, J. O. Hirschfelder, and H. S. Taylor, *J. Chem. Phys.*, **4**, 479 (1936).
(10) H. Eyring, H. Gershinowitz, and C. Sun, *ibid.*, **3**, 786 (1935).
(11) Gorin, *Acta Physicochim. URSS*, **9**, 691 (1938).
(12) (a) E. Gorin, W. Kauzmann, J. Walter, and H. Eyring, *J. Chem. Phys.*, **7**, 633 (1939). (b) For a critique of the Gorin model see H. S. Johnston and P. Goldfinger, *ibid.*, **37**, 700 (1962).

The zero of energy of the system is taken at $r \rightarrow \infty$. The critical internal energy, E_0, for reaction of a nonrotating molecule ($J = 0$) is

$$E_0 = V(r_m) - V(r_e) \tag{3}$$

For a rotating molecule in rotational quantum state J, the critical internal energy is reduced by the difference in rotational energy of the molecule at $r = r_e$ and the activated complex at $r = r_m$.

$$E_0(J) = V_{eff}(r_m) - V_{eff}(r_e) = E_0 +$$

$$E_J(r_m) - E_J(r_e) = E_0 + \frac{J(J + 1)\hbar^2}{2\mu}\left(\frac{1}{r_m{}^2} - \frac{1}{r_e{}^2}\right) \tag{4}$$

In this treatment, the value of r_m, the separation at the top of the barrier, is considered fixed (at some appropriate average value), independent of J. Hence, $E_0(J) < E_0$. It is important to note that for this model to be realistically apt an appropriate condition is that $V(r_m) \gg E_J(r_m)$, or else I^+ is strongly dependent on J.

If the rate constant for $J = 0$ is designated $k(0)$, then the rate constant $k(J)$ for $J > 0$ is

$$k(J) = k(0) \exp\left[-\frac{J(J + 1)\hbar^2}{2\mu kT}\left(\frac{1}{r_m{}^2} - \frac{1}{r_e{}^2}\right)\right] \tag{5}$$

The average rate constant k over all J's is

$$k = \sum_{J=0}^{\infty} k(J)P(J) \tag{6}$$

where

$$P(J) = (2J + 1)\exp[-J(J + 1)\hbar^2/\mu r_e{}^2 kT]/Z_r$$

and

$$Z_r = \sum_{J=0}^{\infty} (2J + 1)\exp[-J(J + 1)\hbar^2/\mu r_e{}^2 kT] \tag{7}$$

On changing the sum to an integral and integrating, we have

$$k/k(0) = Z_r{}^+/Z_r = r_m{}^2/r_e{}^2 \tag{8}$$

Thus the rate constant is enhanced by the ratio of the rigid rotor partition functions for the complex and the molecule. The result is the same as that which would be obtained by invoking the equilibrium assumption of ART theory.

Although the approximate treatment of RG can be (and was) applied to the case of low or vanishing barriers, it was noted above   at the average potential approximation, with fixed r_m, is most closely realized in systems where the potential barrier is large for   he reverse process and therefore only modestly dependent on J. In such a case, bond stretching at the top of the barrier will in general correspond to the lesser end of possible range of $r_m{}^2/r_e{}^2$ values and centrifugal energy effects tend to be small. One example of such a reaction is the dissociation of 3,4,4-trimethylpentyl-2 radical[13]

$$E_{assoc} \sim 12 \text{ kcal mole}^{-1}$$
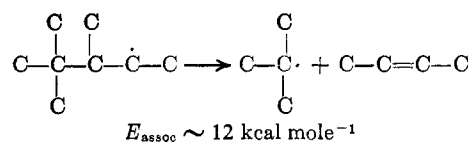
(13) C. W. Larson, Ph.D. Thesis, University of Washington, Seattle, 1969.

B. CASE II. NO BARRIER FOR REVERSE ASSOCIATION REACTION

For unimolecular decomposition reactions whose reverse reaction has "no" barrier to recombination, e.g., radical-radical reactions and ion–molecule reactions, the configuration of the activated complex depends strongly on the rotational quantum state. For a nonrotating molecule there is no hump between the reactant and product and the activated complex lies at an infinite separation between the two fragments.[10] For a rotating molecule, the centrifugal potential is superimposed upon the attractive potential and will usually produce a hump which is the position of the activated complex. In contrast to case I, the value of r_m depends strongly on J (Figure 2). For an attractive potential of the form

$$V(r) = -A/r^s \qquad (s > 2) \qquad (9)$$

the position of the hump can be easily found, as was done by Gorin[12,13] and by Eyring, Hirschfelder, and Taylor,[9] following the method of Eyring, Gershinowitz, and Sun.[10] The repulsive part of the total intermolecular potential is negligible at the relatively large distances of the complex and can be ignored. Again the molecule is treated as a diatomic molecule and the effective potential is given by eq 2. The top of the hump occurs at an interatomic distance, r_m, where

$$dV_{eff}(r_m)/dr = 0 \qquad (10)$$

and

$$d^2V_{eff}(r_m)/dr^2 < 0 \qquad (11)$$

On solving for $V_{eff}(r_m)$

$$V_{eff}(r_m) = \frac{(s-2)}{2}\left[\frac{J(J+1)\hbar^2}{\mu s}\right]^{s/(s-2)} A^{-2/(s-2)} \qquad (12)$$

In the absolute rate theory treatment, a pseudo-rotational partition function for the above energy level scheme was defined as[9-12]

$$Z_r^+ = \sum_{J=0}^{\infty} (2J+1)\exp[-V_{eff}(r_m)/kT] \qquad (13)$$

As was pointed out,[2c] the energy levels, $V_{eff}(r_m)$, are not those for a conventional rotor, but eq 13 is a useful form.

Equation 13 can be integrated to give

$$Z_r^+ = \frac{8\pi^2\mu kT}{h^2}\left\{\Gamma\left(\frac{s-2}{s}\right)\left[\frac{(s-2)A}{2kT}\right]^{2/s}\right\} \qquad (14)$$

Equation 14 has the form of a rigid-rotor partition function if we identify[6,10,14] the quantity in braces with the square of the apparent distance between the centers of masses, i.e., define

$$\langle\langle r_m^2\rangle\rangle = \Gamma\left(\frac{s-2}{s}\right)\left[\frac{(s-2)A}{2kT}\right]^{2/s} \qquad (15)$$

The double angular brackets are used to distinguish between $\langle r_m^2\rangle$, the *average* square of the distance, and $\langle\langle r_m^2\rangle\rangle$, the *apparent* square of the distance.[6,10,14] This distinction is important when a ratio of the rotational partition functions of
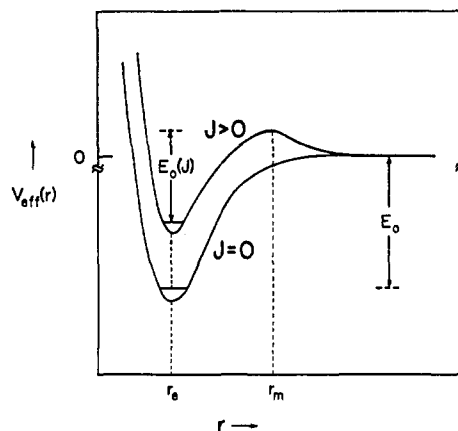

Figure 2. Case II potential energy diagram; the value of r_m depends on the rotational state J.

the activated complex Z_r^+/Z_r to the molecule is expressed as a ratio of the square of the appropriate distances.

$$Z_r^+/Z_r = \langle\langle r_m^2\rangle\rangle/r_e^2 \qquad (16)$$

Tschuikow-Roux[15] has calculated yet another quantity, $\langle r_m\rangle$, the average distance between the centers of masses of the activated complex, which he uses to describe the activated complex. But he inappropriately uses $\langle r_m\rangle^2$ to calculate Z_r^+/Z_r instead of $\langle\langle r_m^2\rangle\rangle$, as in eq 16. The error in using $\langle r_m\rangle^2$ is shown below for $s = 6$, i.e., for a London dispersion force between particles

$$\langle r_m\rangle^2 = 1.714(2A/kT)^{1/3} \qquad (17)$$

$$\langle\langle r_m^2\rangle\rangle = 1.354(2A/kT)^{1/3} \qquad (18)$$

The use of $\langle r_m\rangle^2$ leads to an error of ~25% in the rate constant.

The complete absolute rate theory expression for the unimolecular rate constant is[2d]

$$k^\infty_{uni} = \kappa\frac{kT}{h}\frac{Z_r^+Z_v^+}{Z_rZ_v}\exp(-E_0/kT) \qquad (19)$$

III. Unimolecular Decomposition in the General Pressure Region

A. VARIANTS OF THE MARCUS–RICE TREATMENT

Some confusion has arisen over the treatment of rotations in Marcus–Rice RRKM theory. In particular, the meaning of the term "centrifugal effects" has been used in various manners which may be misleading to the casual reader. To examine the matter, we present the theory in its chronological development with emphasis on the energetics involved; we employ as much of the original notation as is convenient.

1. Treatment of 1951–1952

Marcus and Rice[4,5a] laid the groundwork for RRKM theory in its present form in 1951–1952. In most respects, the assumptions in RRKM theory are the same as those in ART; in both, the reaction rate is proportional to the relative volumes

(14) O. K. Rice, "Statistical Mechanics, Thermodynamics and Kinetics," W. H. Freeman and Co., San Francisco, Calif., 1967, pp 499–502.

(15) E. Tschuikow-Roux, J. Phys. Chem., 72, 1099 (1968).

of phase space accessible to reactants and activated complexes. There is an important distinction, however. Use of "simple" ART theory, with no explicit consideration of angular momentum as in the more sophisticated treatments,[9-12] places no restrictions on overall rotations; rotational states of the activated complex and the molecule are populated according to their equilibrium distribution. In the RRKM theory formal explicit restrictions on the rotational states are introduced.[4] Based on the reasoning of RG, the quantum number J for overall rotations is taken constant during the course of a reaction in order to conserve total angular momentum.

The expression for k_{uni} is

$$k_{uni} =$$

$$\frac{P_1^+ \exp(-E_a/kT)}{P_1 P_2 h} \int_0^\infty \frac{\sum_{Ev^+ \leq E^+} P(E_v^+) \exp(-E^+/kT) \, dE^+}{1 + k_a/\omega} \quad (20)$$

where the microscopic rate constant for molecules of energy $E(= E^+ + E_a)$ is

$$k_a = \frac{P_1^+ \sum_{Ev^+ \leq E^+} P(E_v^+)}{P_1 h N^*(E^+ + E_a)} \quad (21)$$

where E_a is the critical energy of reaction and equals the difference in zero-point energy of the activated complex and molecule (and was denoted in eq 3 as E_0). Here we have limited ourselves to the conventional condition in which all vibrational degrees of freedom are active; the inclusion of *active* internal rotational degrees of freedom in either the activated complex or excited molecule would necessitate more general expressions[6a] but offers no real complication. At high pressure $(\omega \rightarrow \infty)$

$$k^\infty_{uni} = \frac{kT}{h} \frac{P_1^+ P_2^+}{P_1 P_2} \exp(-E_a/kT) \quad (22)$$

in agreement with the ART expression (eq 19); and at low pressures $(\omega \rightarrow 0)$

$$k^0_{uni} =$$

$$\frac{\omega \exp(-E_a/kT)}{P_2} \int_0^\infty N^*(E^+ + E_a) \exp(-E^+/kT) \, dE^+ \quad (23)$$

P_1^+/P_1 is the ratio of overall rotational, *i.e.*, adiabatic, partition functions of the complex and the molecule and simplifies to a ratio of the square root of moments of inertia of the degrees of freedom concerned, together with the appropriate symmetry number ratio. This ratio appears in the total rate constant expression (eq 20) for k_{uni}, and in the expression (eq 21) for k_a, the microscopic specific rate constant for molecules of active energy E. Thus, in the original limiting forms for k_{uni} given by Marcus: (a) as $\omega \rightarrow \infty$, P_1^+/P_1 remains, as is proper; and (b) as $\omega \rightarrow 0$, P_1^+/P_1 cancels out to give a resulting expression which can be correct in numerical magnitude only when $P_1^+/P_1 = \sigma_1/\sigma_1^+$. It is clear that at high pressure the partition function ratio appears for the same reason that it appears in the treatment by RG (eq 8) discussed in an earlier section. At low pressure, however, the absence of P_1^+/P_1 in k_{uni} arises from its appearance in k_a. The rationale for the presence of P_1^+/P_1 in k_a is less explicit: it was assumed that an "equilibrium" exists between the activated complex and its precursor, the excited molecule of internal energy E, and then the intro-

duction by Marcus of the ratio of partition function P_1^+/P_1 was based simply on a reference to the earlier treatment of RG.[5a] This application in the present instance is not adequate; specific consideration of the composition of the total active energy of the activated complex for each state J of the molecule of internal energy E is needed.

2. Treatment of 1962

In 1962, Wieder and Marcus[5b] revised the expression for k_a (eq 21) by omitting from P_1^+/P_1 the ratio $(I_A^+ I_B^+ I_C^+ / I_A I_B I_C)^{1/2}$, although leaving the ratio of symmetry numbers which directly affect the question of the correct definition of reaction path degeneracy. (The ratio of symmetry numbers must appear in the expression for k_a to ensure that all the dissociative states in $\Sigma P(E_v^+)$ have been counted properly.) Then

$$k_a = \frac{\sigma_1 \sum_{Ev^+ \leq E^+} P(E_v^+)}{\sigma_1^+ h N^*(E^+ + E_a)} \quad (24)$$

The above expression, however, is not quite complete. The energy of the molecule, $E^+ + E_a$, does not mesh properly with that of the activated complex, E^+, except for the case of the rigid complex, whose product of moments of inertia is the same as that of the molecule, or for the rotationless state $(J = 0)$. The centrifugal energy of rotating molecules whose product of moments increases in the complex configuration will effectively reduce the critical energy, E_a.

3. Treatment of 1965

In 1965, Marcus[5c] modified k_a in a manner which implicitly rectifies the matching of energy levels just mentioned. The method is accurate and facile. Figure 3 illustrates how the energy levels of the complex were meshed with those of the molecule. The figure is similar to that given by Marcus,[5c] and which continued to employ the RG rigid-rotor model, except that the energy quantities are superimposed on a potential energy diagram. It can be seen that for $J = 0$, eq 24 is obtained, since $E^+ + E_a = E$. But for $J > 0$ the active energy of the molecule is $E = E_a + E^+ + E_J^+ - E_J$. However, this expression is somewhat misleading because the active energy of the molecule, E, is here intermingled with the corresponding adiabatic or centrifugal energies, E_J and E_J^+, although E does not in fact depend on J. (Since the active and adiabatic degrees of freedom are defined to be orthogonal to each other, that is, no energy is allowed to be exchanged between them, there would appear to be a contradiction in terms.) Nonetheless, if we take note of the fact that the centrifugal energy is being added to the potential energy, then we can interpret the Marcus expression as representing the centrifugal energy lowering of the critical energy of the rotationless state, called here E_a, to an effective critical energy, $E_a + E_J^+ - E_J$ (identical with eq 4 in an earlier section). Then k_{EJ}, the specific rate constant for a molecule in rotational state J with internal energy E, is

$$k_{EJ} = \frac{\sigma_1 \sum_{Ev^+ \leq E^+} P(E_v^+)}{\sigma_1^+ h N^*(E^+ + E_J^+ - E_J + E_a)} \quad (25)$$

Marcus[5c] defined a quantity, $E^* = E^+ + E_a$, to simplify the expressions. Such a definition, however, tends to obscure the relationship between E and E^+ so we have omitted this substitution in our expressions. Since the variable in the rate

constant integral (eq 20) is E^+, we express k_a in terms of this quantity. An approximate method was employed to average k_{EJ} over all J's. First E_J^+ and E_J were averaged over all J's and found to be[5c] $\langle E_J^+ \rangle = lkT/2$ and $\langle E_J \rangle = (I^+/I)lkT/2$, respectively, where l is the number of adiabatic rotations under consideration (usually $l = 2$). Next these average values were inserted in eq 25 to obtain some average k_a. Finally, a factor F was introduced to relate eq 24 to eq 25. Define

$$F = \frac{N^*(E^+ + E_a + \langle E_J^+ \rangle - \langle E_J \rangle)}{N^*(E^+ + E_a)} \qquad (26a)$$

$$= \frac{N^* (E^+ + E_a - lkT[I^+ - I]/2I)}{N^*(E^+ + E_a)} \qquad (26b)$$

As a first approximation, F is constant with increasing E^+ at the energy in question. The corrected expression for k_a is then

$$k_a = \frac{\sigma_1 \sum\limits_{E_v^+ \le E^+} P(E_v^+)}{\sigma_1^+ h N^*(E^+ + E_a)F} \qquad (27)$$

Equation 27 can now be inserted in eq 20 to make calculations which take explicit account of centrifugal effects. For example, $F = 0.8$ for ethane decomposition. A typographical error in Marcus' expression for F (eq 26b) has been perpetuated in recent papers:[16-18] a plus sign appeared in front of lkT (ref 5c, eq 8) instead of the correct minus sign.

As mentioned above, at high pressure the result for k_{uni} is the same as that given previously (eq 22). But now at low pressures, $\omega \to 0$, the result is

$$k^0{}_{uni} =$$

$$F\left(\frac{I_A^+ I_B^+ I_C^+}{I_A I_B I_C}\right)^{1/2} \frac{\omega \exp(-E_a/kT)}{P_2} \int_0^\infty N^*(E^+ +$$

$$E_a) \exp(-E^+/kT) \, dE^+ \qquad (28)$$

Thus, eq 28 adds a factor $F(I_A^+ I_B^+ I_C^+/I_A I_B I_C)^{1/2}$ to the original formulation for $k^0{}_{uni}$ (eq 23).

4. Remarks

Various connotations have been attached in the literature to the 1952 MR treatment and to the extent to which it correctly embodies centrifugal effects.[4,5a,16-18] It is clear from Table I that centrifugal effects *do* enter correctly into the treatment of $k^\infty{}_{uni}$ but not of $k^0{}_{uni}$: the high-pressure rate constant in I is unaffected by refinements offered in II and III, but only in III was the correct (approximate) form of $k^0{}_{uni}$ obtained.

Contrary to several assertions,[16,17] the centrifugal effect is larger at $p = \infty$ than at $p = 0$ and declines between these limits by the factor F, which is necessarily less than unity.

B. MORE EXACT CALCULATIONS AT LOW PRESSURE

Detailed calculations of the centrifugal effect at the high- and low-pressure limits have been performed recently by Forst.[19]

(16) M. C. Lin and K. J. Laidler, *Can. J. Chem.*, **46**, 79 (1968).

(17) E. Tschuikow-Roux, *J. Chem. Phys.*, **49**, 3115 (1968).

(18) In ref 16 it is not clear what was done: an incorrect sign was used although F was given its conventional magnitude, *i.e.*, less than unity; however, the final numerical magnitude of the rate constant given appears to be corrected in the right direction. In ref 17 an incorrect sign is employed which affects some deductions and description of the C_2F_6 system; further comment on this system will be given later.

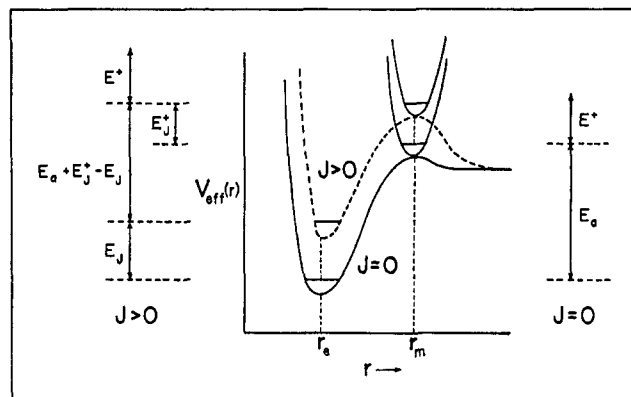(19) W. Forst, *J. Chem. Phys.*, **48**, 3665 (1968).

Figure 3. Diagram of energy levels of the molecule and the complex superimposed on the potential energy. A slight (fictitious) hump is shown at r_m in order to lend plausibility to the assumption of a constant value of r_m, *i.e.*, I^+, independent of J.

In one approach, a treatment was given that is essentially that of RG and expressions of the form of eq 25 were used. At high pressure, the conventional contribution to k_∞ was obtained as given in eq 8 and 22.

At low pressure, k_{uni}, given by Marcus–Rice,[5c] takes the form

$$k^0{}_{uni} = \frac{\omega}{P_2} \int_0^\infty \int_{E_a J}^\infty P(J) N^*(E) e^{-E/kT} \, dE \, dJ \qquad (29)$$

where $E_a{}_J = E_a - E_J + E_J^+$. A simple analytical form for this double integral does not exist. Approximate expressions for its evaluation were introduced by Forst so that a computation could be made for a case I potential, with constant value of I^+, by the use of standard integral tables. We prefer a straightforward approach of numerical evaluation of eq 29 after rewriting it in alternate form; this is simple and direct, and also eliminates some error in the approximations as used by Forst. Consider first the case I potential function of Figure 1. The critical energy is given by eq 4. The approach is relatively straightforward since I^+ is not a function of J. We divide the integral in eq 29 for the rate constant into two parts: one includes the fraction of molecules in all rotation states with vibrational (internal) energy above E_a, and the second is the portion of molecules with vibrational energy below E_a but whose centrifugal energy is sufficient to compensate for the vibrational energy deficit

$$k^0{}_{uni} =$$

$$\frac{\omega}{P_2}\left[\int_{E_a}^\infty N^*(E) e^{-E/kT} \, dE + \int_0^{E_a} N^*(E) f(E) e^{-E/kT} \, dE\right] \qquad (29a)$$

where $f(E)$ is the fraction of molecules at active internal energy E whose centrifugal energy, $E_J - E_J^+$, makes up the "deficit" $E_a - E$. We make the rigid diatomic complex approximation again. Then, ignoring constants which cancel, the low-pressure centrifugal factor is

$$f_0 = \frac{\displaystyle\int_{E_a}^\infty N^*(E) e^{-E/kT} \, dE + \int_0^{E_a} N^*(E) f(E) e^{-E/kT} \, dE}{\displaystyle\int_{E_a}^\infty N^*(E) e^{-E/kT} \, dE} \qquad (29b)$$

Table I

Interrelation of Centrifugal Factors in Various RRKM Rate Formulations

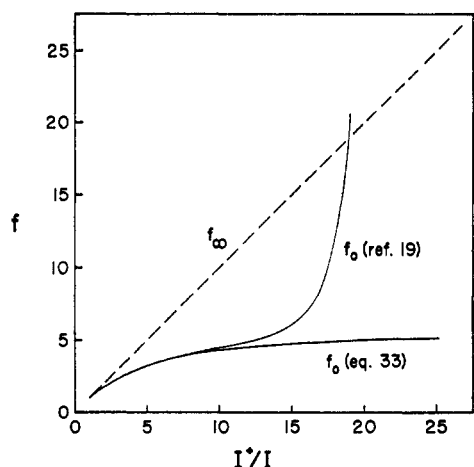|	*I (1952)*[5a]	*II (1962)*[5b]	*III (1965)*[5c]
k^{∞}_{uni}	$(I_A{}^+I_B{}^+I_C{}^+/I_AI_BI_C)^{1/2}$	$(I_A{}^+I_B{}^+I_C{}^+/I_AI_BI_C)^{1/2}$	$(I_A{}^+I_B{}^+I_C{}^+/I_AI_BI_C)^{1/2}$
k^0_{uni}	1	$(I_A{}^+I_B{}^+I_C{}^+/I_AI_BI_C)^{1/2}$	$F(I_A{}^+I_B{}^+I_C{}^+/I_AI_BI_C)^{1/2}$
k_a	$(I_A{}^+I_B{}^+I_C{}^+/I_AI_BI_C)^{1/2}$	1	F^{-1}

Figure 4. Description of f_{∞} and a comparison of f_0 calculated from eq 33 and f_0 from ref 19, as a function of I^+/I.

Define n_E to be the rotational quantum number such that

$$E_a - E = (n_E(n_E + 1)\hbar^2/2)[I^{-1} - I^{+-1}] \qquad (30)$$

The fraction of all molecules having rotational states above n_E is

$$f(E) = \sum_{J=n_E}^{\infty} (2J + 1) \exp[-J(J + 1)\hbar^2/2IkT]/Z_r \qquad (31)$$

On changing the variable in eq 31 from J to $J(J + 1)$, integrating, and substituting for n_E from eq 30, we have

$$f(E) = \exp[-(E_a - E)I^+/(I^+ - I)kT] \qquad (32)$$

Equation 32 is then substituted in eq 29b, whence

$$f_0 = 1 +$$

$$\frac{\displaystyle\int_0^{E_a} N^*(E) \exp\{[-E - (E_a - E)I^+/(I^+ - I)](kT)^{-1}\} \, dE}{\displaystyle\int_{E_a}^{\infty} N^*(E) \exp(-E/kT) \, dE}$$

$$(33)$$

Equation 33 can be easily solved numerically for f_0 with the use of realistic expressions[20] for $N^*(E)$.

In the case for which $N^*(E)$ is constant, *e.g.*, the harmonic diatomic molecule, eq 33 may be integrated analytically to give the limiting result,[19] $f_0{}^{di} = I^+/I$. It is evident that the centrifugal effect is independent of pressure for this case. It is clear, also, that the Marcus F factor in eq 26 assumes the value of unity when $N^*(E)$ is constant, so that the same result

is obtained. Finally, for this special case the magnitude of the centrifugal effect is independent of the pressure regime. Since, in reality, $N(E)$ declines in general with decrease of E, it follows that the maximum value of f_0 is then constrained to be less than f_{∞}.

In the approximations used by Forst[19] for the calculation of f_0 for the case I potential, there is an inaccuracy at relatively large values (>10) of I^+/I which appears in the illustration offered by him for the case of methyl chloride decomposition: f_0 increases with increase of the ratio I^+/I and eventually becomes larger than the centrifugal contribution at high pressure; indeed, it appears to rise asymptotically to infinity at $I^+/I \sim 20$ (Figure 4). The present calculations show instead that f_0 first rises with increasing I^+/I and then tends to level off at a value less than f_{∞}.

An alternate method for the evaluation of eq 29 was described by Hay and Belford[21] using the semiclassical[4,5,20] expression for $N^*(E)$. The result for f_0 was expressed as a double sum over a series. The rigorous solution is somewhat onerous, and an approximate form was given in terms of an F factor as

$$F_b = \exp[-(n' - 1)(I^+/I - 1)RT/(E_a + E_z + RT)] \qquad (34)$$

where n' is the total number of vibrational degrees of freedom of the excited molecule and E_z is the vibrational zeropoint energy; then, $f_0 = F_bI^+/I$. The results using eq 34 agree satisfactorily for small values of I^+/I with those obtained from eq 33; however, the calculated f_0 passes through a maximum with increasing I^+/I at $I^+/I = (E_a + E_z + RT)/(n' - 1)RT$, contrary to the prediction of eq 33.

A different approximate formula has been derived[22] by us using eq 33 as a starting point and expressing $N^*(E)$ again in its semiclassical form; the expression is

$$F_w = [1 + (n' - 1)(I^+/I - 1)RT/(E_a + aE_z)]^{-1} \qquad (35)$$

The factor, a, multiplying E_z is the quantum correction to the semiclassical densities.[20a]

The values of f_0 from eq 33 may be compared with those from F (Table I), from F_b, and from F_w. This we shall do after considering a case II potential where I^+ should realistically depend on J.

For a case II potential (Figure 2), a linear relationship between $n_E(n_E + 1)$ and E, as in eq 30, no longer exists. From eq 12 we have instead

$$E_a - E = \frac{n_E(n_E + 1)\hbar^2}{2I} -$$

$$\frac{s - 2}{2}\left[\frac{n_E(n_E + 1)\hbar^2}{\mu s}\right]^{s/(s-2)} A^{-2/(s-2)} \qquad (36)$$

It is not feasible to substitute E for n_E in $f(E)$ although analytic expressions do exist for $s = 3, 4$, and 6. It is simpler instead to

(20) (a) G. Z. Whitten and B. S. Rabinovitch, *J. Chem. Phys.*, **41**, 1883 (1964); D. C. Tardy, B. S. Rabinovitch, and G. Z. Whitten, *ibid.*, **48**, 1427 (1968); (b) E. Thiele, *ibid.*, **39**, 3258 (1963); (c) W. Forst, Z. Prasil, and P. St. Laurent, *ibid.*, **46**, 3736 (1967).

(21) A. J. Hay and R. L. Belford, *ibid.*, **47**, 3944 (1967).

(22) E. V. Waage and B. S. Rabinovitch, *ibid.*, in press.

Table II

Comparison of Low-Pressure Centrifugal Factors for Ethane Decomposition (T = 600°K)

| I^+/I | F | Case I potential | | | | Case II potential | | |
		FI^+/I	F_bI^+/I	F_wI^+/I	f_0 (eq 33)	f_0 (eq 38)	F_dI^+/I	F_d
1	1.000	1.00	1.00	1.00	1.00	1.00	1.00	1.00
2	0.850	1.70	1.71	1.72	1.72	1.75	1.72	0.861
3	0.719	2.16	2.19	2.27	2.26	2.37	2.29	0.763
4	0.608	2.44	2.49	2.70	2.68	2.86	2.70	0.676
6	0.432	2.60	2.72	3.34	3.28	3.57	3.17	0.528
8	0.306	2.45	2.64	3.78	3.69	4.06	3.29	0.411
10	0.214	2.14	2.41	4.10	3.99	4.40	3.26	0.326

make a change of variable and solve numerically in a manner similar to that used by Forst[19] for a case II potential. Let $x = n_E(n_E + 1)\hbar^2/2I$ and

$$a = \frac{s-2}{2}\left(\frac{2r_e^2}{s}\right)^{s/(s-2)} A^{-2/(s-2)}$$

then from eq 36

$$E_a - E = x - ax^{s/(s-2)} \qquad (37)$$

If we change the variable in the second integral in the numerator of eq 29b from E to x, then $f(x) = e^{-x/kT}$, and eq 38 results.

$$f_0 = 1 - \left\{ \int_0^\infty N^*(E_a - x + ax^{s/(s-2)}) \exp[-(E_a - x + $$

$$ax^{s/(s-2)})/kT]\{[as/(s-2)]x^{2/(s-2)} - 1\}e^{-x/kT}\,dx\right\} \Big/$$

$$\int_{E_a}^\infty N^*(E)e^{-E/kT}\,dE \qquad (38)$$

The minus sign appears since the limits of integration were interchanged; f_0 is still greater than unity. The upper limit of integration is actually finite, but very large, because we disallow the highly excited rotational states where $r_m \sim r_e$ in this formulation. Minor error results since these higher states have low probability; in any event, this artifactual error is relatively larger only for the unimportant condition of I^+/I approaching unity.

For the purpose of the present critique, calculations were performed by using eq 38 with $s = 6$; good agreement of eq 33 with eq 38 is obtained if the "apparent" moment of inertia $I^+ = \mu\langle\langle r_m^2\rangle\rangle$ (eq 15) is used in eq 33. Results of these calculations along with a comparison of the several approximations to the low-pressure centrifugal factor are illustrated in Table II for ethane decomposition, $C_2H_6 \to 2CH_3$, for a series of assumed values of I^+/I. The moments of inertia in question are with respect to the pair of equal principal axes.

For small values of I^+/I (*i.e.*, from 1 to 4), Marcus' expression, FI^+/I, agrees within 10% with f_0 calculated from eq 33. Above a ratio of 4, the agreement rapidly worsens. F_w gives the best, and very good agreement over the entire range. Finally, the agreement between eq 33 and 38 is good ($\sim$10%) over the entire interesting range of I^+/I.

For the case II potential where I^+ depends on J, a different average over J is necessary[23] for calculating an F factor. The average rotational energies have been calculated in the section

on Bimolecular Association (eq 52 and 53). Inserting them in eq 26a, we have for the case $s = 6$ (dispersion force)

$$F_d = \frac{N^*(E^+ + E_a - kT[0.730I^+/I - 0.667])}{N^*(E^+ + E_a)} \qquad (39)$$

F_d can then be inserted in eq 27 in place of F. On comparing F_dI^+/I with f_0 (eq 38) in Table II, good agreement is found, but even better agreement is found between F_wI^+/I and this f_0.

Since the expressions for F, F_w, and F_d are easy to use, we wish to establish a rule of thumb for the range of their validity. To do so we have compared FI^+/I, F_dI^+/I, and F_wI^+/I with f_0 from eq 33 (the conclusions with regard to eq 38 are then obvious) using classical densities for n (effective) oscillators. We use classical densities only for their utility in making comparisons. Figure 5 shows plots of the maximum value of I^+/I which can be used in F and F_d for attendant errors of 10%. For larger I^+/I values, the agreement with eq 33 worsens. A curve for F_w does not appear in the figure since the error is nowhere as large as 10% (usually 3% or less).
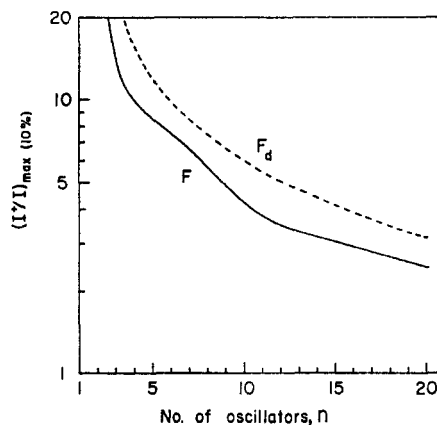

Figure 5. Plot of maximum values of I^+/I on a log scale for a molecule having n classical oscillators for which F, or F_d, give agreement between FI^+/I, or F_dI^+/I, and f_0 (eq 33), with an error of 10%. A curve for F_wI^+/I is off the graph since the errors are everywhere below 10% (*e.g.*, for $I^+/I = 10$, the maximum error is 2% at all n, and, by contrast with the behavior shown, the error decreases with increase in n).

In any case, a modified optimum correction factor can be found by taking a value to be that which gives agreement with f_0 from eq 33 (and hence also eq 38), *i.e.*, $F_0 = f_0I/I^+$. This definition also brings the modified average correction into good agreement with the falloff behavior considered next.

(23) R. A. Marcus, private communication.

Table III

Case I Potential. Some Comparison of Falloff (k/k_∞) Calculations for Ethane

Log P, Torr	I^+/I 2		4		6		8	
	Exact[a]	F_0[b]	Exact	F_0	Exact	F_0	Exact	F_0
5	0.999	1.000	0.999	1.000	0.999	1.000	0.996	0.999
4	0.996	0.997	0.996	0.996	0.992	0.996	0.983	0.995
3	0.976	0.976	0.967	0.970	0.951	0.965	0.928	0.960
2	0.868	0.869	0.838	0.848	0.799	0.828	0.757	0.812
1	0.596	0.595	0.548	0.558	0.501	0.527	0.459	0.501
0	0.266	0.265	0.232	0.236	0.204	0.214	0.181	0.196
−1	0.0742	0.0738	0.0619	0.0626	0.0529	0.0547	0.0462	0.0487
−2	0.0142	0.0141	0.0115	0.0116	9.68×10^{-3}	9.86×10^{-3}	8.36×10^{-3}	8.60×10^{-3}
−3	2.12×10^{-3}	2.10×10^{-3}	1.69×10^{-3}	1.69×10^{-3}	1.40×10^{-3}	1.41×10^{-3}	1.20×10^{-3}	1.22×10^{-3}
−4	2.66×10^{-4}	2.64×10^{-4}	2.10×10^{-4}	2.09×10^{-4}	1.73×10^{-4}	1.73×10^{-4}	1.47×10^{-4}	1.47×10^{-4}

[a] Calculated from eq 40.　[b] $F_0 = f_0 I/I^+$.

Table IV

Case II Potentials. Some Comparison of Falloff (k/k_∞) Calculations for Ethane

Log P, Torr	I^+/I 2		4		6		8	
	Exact[a]	F_0[b]	Exact	F_0	Exact	F_0	Exact	F_0
3	0.977	0.976	0.972	0.972	0.964	0.968	0.954	0.963
1	0.602	0.598	0.565	0.568	0.529	0.540	0.494	0.516
0	0.271	0.268	0.242	0.244	0.218	0.223	0.197	0.206
−1	0.0760	0.0747	0.0652	0.0654	0.0569	0.0580	0.0480	0.0520
−2	0.0146	0.0143	0.0122	0.0122	0.0104	0.0106	9.07×10^{-3}	9.29×10^{-3}
−3	2.18×10^{-3}	2.13×10^{-3}	1.79×10^{-3}	1.79×10^{-3}	1.51×10^{-3}	1.52×10^{-3}	1.30×10^{-3}	1.32×10^{-3}
−4	2.76×10^{-4}	2.69×10^{-4}	2.33×10^{-4}	2.23×10^{-4}	1.87×10^{-4}	1.87×10^{-4}	1.60×10^{-4}	1.61×10^{-4}

[a,b] As in Table III.

The remaining discussion will be given in terms of F_0 rather than F_w, since F_0 is an optimum factor. As a matter of practical facility, F_w could be employed rather than F_0 with only minimal loss of accuracy.

C. MORE EXACT CALCULATIONS IN THE FALLOFF REGIME

The centrifugal effect in the falloff pressure regime is more difficult to calculate since there are no simplified expressions; a laborious double integration must be performed. The rate constant[5c] is shown in eq 40, where $P(J) = (2J + 1)$ exp$(-E_J/kT)/P_1$.

$$k_{uni} = \frac{\exp(-E_a/kT)}{P_2 h} \times$$

$$\int_0^\infty \int_0^\infty \frac{\sum_{E_v^+ \leq E^+} P(E_v^+) P(J) \exp[(-E^+ + E_J - E_J^+)/kT]}{1 + k_{EJ}/\omega} dE^+ dJ \quad (40)$$

Rate constants for ethane decomposition at 600°K have been calculated using eq 40 for both case I (Figure 1) and case II (Figure 2) potentials and were compared with those from eq 20, using both Marcus' F factor (eq 26 and 27) and the improved factor, $F_0 = f_0 I/I^+$, in k_a. Since use of the improved factor necessarily yields the same results as eq 40 in both the high- and low-pressure limits, present comparisons are restricted to this factor. Results are shown in Table III for a case I potential (constant r_m), and in Table IV for a case II r^{-6} po-

tential; k/k_∞ is tabulated at different pressures for several illustrative values of I^+/I (for the case II potential, $I^+/I = \langle\langle r_m^2\rangle\rangle/r_e^2$).

It is seen that use of the improved F_0 factor results in agreement with eq 40 to within a maximum deviation of 5% at intermediate falloff, for I^+/I as large as 6 for a case I potential (Table III), and for I^+/I as large as 8 for a case II potential[24] (Table IV). Since values of I^+/I greater than 6–8 are seldom encountered, the F_0 factor may be used for accurate falloff calculations. Although this observation is based on calculations with only one model, C_2H_6, other models are expected to behave similarly. Furthermore, the deviation just noted does not result in a formal change in the average description of falloff behavior. The shapes of falloff curves of log (k/k_∞) vs. log P are altered slightly by using the F_0 factor as compared with the shapes using eq 40. However, since agreement is required for k_{uni}^∞ and for k_{uni}^0 there is virtually no change in the description of the average behavior so that n, the Slater number[25] of oscillators, is practically invariant.

The use of the original Marcus F factor will result in similar agreement with eq 40 insofar as it agrees with the F_0 factor, i.e., f_0 in Table II. In any case, at high pressure, all treatments agree.

It is important to note that use of an F or F_0 factor in k_a (eq 27) does not change the shape of the log–log falloff curve as

(24) At the limiting low pressures for $I^+/I = 2$ for a case II potential, the two sets of values disagree slightly owing to small differences in the normalizations used.

(25) N. B. Slater, "Theory of Unimolecular Reactions," Cornell University Press, Ithaca, N. Y., 1959, pp 150, 168.

compared with the Marcus-Rice original 1951-1952 formulation.

The only centrifugal calculations that describe detailed fall-off behavior (k/k^{∞}_{uni} vs. p) appear to be those of Tschuikow-Roux[17] for C_2F_6 decomposition. The Marcus F factor was used, but because of an incorrect sign in the equation, his value of F was greater than unity (4.89 by our estimate) and consequently the centrifugal effect was computed to be much *larger* at the low-pressure limit than at high pressure. In addition, in this calculation an incorrect moment of inertia expression was applied to the evaluation of f_0, a value of ~ 140 was apparently used, and a very large incorrect pressure displacement was generated. By using eq 33 (since Marcus' F factor is inaccurate for the large ratio $I^+/I \simeq 5$ used), a more correct value of f_0 of only 1.88 is found. The centrifugal effect corrections are very much less than was concluded by Tschuikow-Roux.

IV. Activation Energy Considerations

In general, the centrifugal effect contributes to the observed Arrhenius activation energy E_A for unimolecular reactions only to a small extent.

At high pressure, there is no effect on the activation energy for a case I potential but there is for a case II potential. Since $\langle\langle r_m^2\rangle\rangle$, and hence k^{∞}_{uni}, varies as $(kT)^{-2/s}$ (eq 15), then a term $(2/s)kT$ is subtracted from the case I value of E_A^{∞}. It is evident that the statement made above that all reaction rate models give the same result for k^{∞}_{uni}, wherein the factor I^+/I appears, is correct insofar as the proper value of I^+ is used. The latter is perhaps more appropriately written as $I^+(T)$ for the case II potential inasmuch as I, which is temperature dependent only in the sense of failure of the conventional rigid rotor model of the molecule, shows much weaker temperature dependence.

At the low-pressure limit, there will also be a small activation energy effect for both case I and II potentials. There is no simple analytical form for this effect for a case II potential, but expressions have been given by Hay and Belford[21] for a case I potential; one approximate form obtained by them with use of F_b was

$$\Delta E^0_{A \ (rot)} = -(n' - 1)(I^+/I - 1)(RT)^2/(E_a + E_a + RT) \quad (41)$$

Our expression for F_w leads to an improved result

$$\Delta E^0_{A \ (rot)} = -(n' - 1)(I^+/I - 1)(RT)^2/[E_a +$$

$$aE_a + (n' - 1)(I^+/I - 1)RT] \quad (42)$$

Values obtained from eq 41 and 42 for various assumed values of I^+/I are compared with an "exact" result for ethane decomposition obtained by taking $-d \ln f_0/d(1/RT)$ where f_0 is found from eq 33. Good agreement (~ 0.01 kcal) is found between the exact results and those from eq 42 (Table V).

The negative sign of $\Delta E^0_{A \ (rot)}$ means that the measured activation energy is lowered relative to the value that would obtain if $I^+ \equiv I$.

Equation 42 can also be used for a case II potential insofar as f_0 (case II) would be expected to mimic the temperature dependence of f_0 (case I).

Table V

Contribution to the Arrhenius Activation Energy from Overall Rotations at Low Pressure for Ethane Decomposition

| I^+/I | $-\Delta E^0_{A \ (rot)}$, kcal mole^{-1} | | |
	Exact[a]	Eq 41[a]	Eq 42[a]
2	0.25	0.29	0.25
3	0.42	0.59	0.42
4	0.55	0.88	0.55
6	0.72	1.47	0.73
8	0.84	2.05	0.85
10	0.94	2.64	0.94

[a] Average of $\Delta E^0_{A(rot)}$ at 600° (873.2°K).

V. Bimolecular Association at High Pressure

A. CROSS SECTIONS

The bimolecular association rate constant for the reverse of unimolecular decomposition can be related to its unimolecular counterpart through the equilibrium constant: $K_{eq} = k_{uni}/k_{bi}$. If k_{bi} is cast into the simple collision form

$$k_{bi} = \sigma^2\left(\frac{8\pi kT}{\mu}\right)^{1/2} \exp(-E_r/kT) \quad (43)$$

where E_r is a critical threshold value of relative translational energy parallel to the line of centers and σ is the collision diameter (hard sphere), then it can be shown[1a] that the moment of inertia of the activated complex for the unimolecular decomposition is given by

$$I^+ = \mu\sigma^2 \quad (44)$$

Use of a hard-sphere collision diameter implies use of a case I potential. We thus identify σ with the ART activated complex distance r_m (Figure 1) given by $I^+ = \mu r_m^2$.

Even more striking is the correspondence[6-8] between collision theory and ART for a case II potential. We follow the treatment by Yang and Ree[6] in presenting an analysis of the two theories with emphasis on the cross sections obtained.

Using eq 9 as the form of the attractive potential between two molecules, the critical impact parameter, $b_c(g)$, as a function of total relative velocity, g, is

$$b_c(g) = [A(s - 2)/\mu g^2]^{1/s}[s/(s - 2)]^{1/2} \quad (45)$$

The reaction cross section is πb_c^2; if it is multiplied by $gh(g)$, where $h(g)$ is the distribution function of relative velocities, and averaged over all g, we have the bimolecular rate constant (ignoring symmetry numbers)

$$k_{bi} = \int_0^{\infty} \pi b_c^2(g)gh(g) \ dg \quad (46)$$

When eq 46 is equated with eq 43 without the exponential involving the critical energy, i.e.

$$\pi\langle b_c^2(g)g\rangle = \pi\sigma^2\langle g\rangle \quad (47)$$

then Yang and Ree showed that

$$\sigma^2 = \langle b_c^2(g)g\rangle/\langle g\rangle = \langle\langle r_m^2\rangle\rangle \quad (48)$$

where $\langle\langle r_m^2\rangle\rangle$ is the apparent ART distance between activated complex mass centers (eq 15). Thus, the formal analogy be-

tween simple collision theory and ART is extended to include cases where more complex potentials are used.

The above derivations are based on high-pressure conditions where the equilibrium assumption can be made. For centrifugal effect calculations of k_{bi} in the falloff or low-pressure regime, the relationship $k_{bi} = k_{uni}/K_{eq}$ can be used along with the expressions for k_{uni} developed earlier in this paper.

B. ROTATIONAL ENERGIES FOR A CASE II POTENTIAL

Some interesting aspects of average rotational energies are now considered. The energies are derived for bimolecular reactions using the diatomic molecule approximation, but the equilibrium results apply also to the reverse unimolecular decompositions. We continue to employ the symbol E_J for rotational energy even though the averaging will be over impact parameters, b, and relative velocities, g.

The rotational energy at $r = r_m$ is

$$E_J = \mu g^2 b^2 / 2r_m^2 \tag{49}$$

When averaged over all g and b and normalized by k_{bi}, then

$$\langle E_J \rangle_{r=r_m} = \int_0^\infty \int_0^{b_c(g)} E_J 2\pi g b h(g) \, db \, dg / k_{bi} = kT \tag{50}$$

To obtain $\langle E_J^+ \rangle$, the average rotational energy at the activated complex distance above the zero of energy (at infinite separation between the colliding species), it is necessary to add to $\langle E_J \rangle_{r=r_m}$ the average potential energy at $r = r_m$

$$\langle V(r_m) \rangle =$$

$$\int_0^\infty \int_0^{b_c(g)} V(r_m) 2\pi g b h(g) \, db \, dg / k_{bi} = -2kT/s \tag{51}$$

Then from eq 50 and 51

$$\langle E_J^+ \rangle = [(s - 2)/s]kT \tag{52}$$

$$= 0.667kT, \text{ for } s = 6$$

To determine $\langle E_J \rangle$, the average rotational energy at $r = r_e$, an average of $E_J = \mu g^2 b^2 / 2r_e^2$ is taken in a manner similar to that in eq 50 and 51

$$\langle E_J \rangle = \left(\frac{s}{s-2}\right) \frac{\Gamma\left(\dfrac{2s-4}{s}\right)kT}{\Gamma\left(\dfrac{s-2}{s}\right)r_e^2} \left[\frac{(s-2)A}{2kT}\right]^{2/s} \tag{53}$$

$$= f_s kT \langle\langle r_m^2 \rangle\rangle / r_e^2$$

$$= 0.730kT I^+/I, \text{ for } s = 6$$

where

$$f_s = \left(\frac{s}{s-2}\right)\Gamma\left(\frac{2s-4}{s}\right) \Big/ \left[\Gamma\left(\frac{s-2}{s}\right)\right]^2 \tag{54}$$

Here $f_s < 1$, as opposed to the result for a case I potential where $\langle E_J \rangle = kT r_m^2/r_e^2 = kT I^+/I$ (for two degrees of freedom, i.e., $l = 2$). Also the value of $\langle E_J^+ \rangle$ given by eq 52 for a case II potential is less than the corresponding value $\langle E_J^+ \rangle = kT$ for a case I potential.

These distinctions are necessary if calculations involving rotational energies are made. For example, Benson[26] has made

(26) S. W. Benson, J. Amer. Chem. Soc., 91, 2152 (1969).

calculations of the rotational energy of ethane (from methyl radical recombination) based on a hard-sphere model (case I potential). But as seen above, such a calculation yields an overestimate for both $\langle E_J^+ \rangle$ and $\langle E_J \rangle$ if there is no critical energy for the association, so that a case II potential is indicated.

Alternative to eq 52 and 53, the rotational energies averaged[23] over J are conveniently interrelated as shown in eq 55, where V_{eff} is given in eq 2.

$$\langle E_J^+ \rangle - \langle E_J \rangle =$$

$$\frac{\displaystyle\int_0^\infty \frac{J(J+1)\hbar^2}{2\mu}\left(\frac{1}{r_m^2} - \frac{1}{r_e^2}\right) \exp[-V_{eff}(r_m)/kT](2J+1)\,dJ}{\displaystyle\int_0^\infty \exp[-V_{eff}(r_m)/kT](2J+1)\,dJ} \tag{55}$$

VI. Glossary of Symbols

A	attractive potential constant
b	impact parameter
$b_c(g)$	critical impact parameter at relative velocity g
E_a, E_0	equivalent symbols for the critical energy (the activation energy at $0\,°K$) of dissociation
$E_0(J)$	same as E_0 for overall rotational quantum state J
$E_J(r)$, E_J, E_J^+	overall rotational energy at the separations between mass centers of $r = r$, r_e, and r_m, respectively
E_v^+	energy of the active vibrations (and internal rotations when included) in the activated complex
E_{assoc}, E_r	same as E_a except for reverse association reaction
E, E^+	energy of the active modes of the excited molecule and the activated complex in excess of their zeropoint energies, respectively
I, I^+	principal moment of inertia for the excited molecule and the activated complex, respectively
I_x, I_x^+	moment of inertia of the excited molecule and the activated complex, respectively, along the X axis.
k_a	specific microscopic rate constant
k_{uni}, k^∞_{uni}, k^0_{uni}	Unimolecular rate constant at general, high, and low pressures, respectively
k_{bi}	bimolecular rate constant
k_{EJ}	same as k_a but for rotational state J
$k(J)$	same as k^∞_{uni} but for rotational state J
l	number of overall rotational degrees of freedom taken as adiabatic (usually $l = 2$)
$N^*(E)$	density of states of active modes of the excited molecule at energy E
P_1, P_1^+	partition functions of the adiabatic modes of the excited molecule and of the complex, respectively
P_2, P_2^+	partition functions of the active modes of the excited molecule and of the complex, respectively
$P(J)$	normalized probability of rotational state J
r	distance between mass centers during the course of a reaction
r_e	equilibrium value of r in the excited molecule

r_m	value of r in the activated complex configuration	σ_2, σ_2^+	symmetry numbers of all other rotations
$\langle\langle r_m^2 \rangle\rangle$	apparent (not average) square of r_m for the case where r_m depends on J	$V(r)$	attractive potential
$\sum_{E_v^+ \leq E^+} P(E_v^+)$	sum of states of active modes of the activated complex at energy E^+	$V_{eff}(r)$	effective attractive potential, including the rotational potential $V_{eff}(r) = V(r) + E_J(r)$
σ_1, σ_1^+	symmetry numbers for adiabatic rotation of the excited molecule and activated complex, respectively	Z_r, Z_r^+	overall rotational partition functions of the excited molecule and the activated complex, respectively
		ω	specific collision rate per unit time