

On the theory of energy distributions of products of molecular beam reactions involving transient complexes*

R. A. Marcus

Department of Chemistry, University of Illinois, Urbana, Illinois 61801
(Received 14 October 1974)

Theoretical energy distributions of reaction products in molecular beam systems are described for reactions proceeding via transient complexes. Loose and tight transition states are considered for the exit channel. For a loose transition state and the case of $l > j$, the result is the same as of Saffron *et al.* For the case of a tight transition state exit channel effects are included analogous to steric effects for the reverse reaction. It is shown how, via one mechanism, bending vibrational energy of that transition state can contribute to the translational energy of the reaction products. Expressions are derived for the energy distributions of the products when $l > j$ and $j > l$.

I. INTRODUCTION

In recent years illuminating experiments on the behavior of long-lived collision complexes have been performed in molecular beam systems.^{1,2} The overall reaction can be represented as



where ABC^* is the long-lived collision complex and ABC^\ddagger is the transition state for the "exit" channel forming $AB + C$. [The transition state for Eq. (1.1) has been omitted for brevity.] In these experiments the translational energy distribution of the reaction products was measured. In related experiments on some of these systems vibrational³ and rotational⁴ energy distributions of the reaction products have also been measured.

Comparison with the data has been made with an adaptation of RRKM theory for both "loose" and "tight" transition states, as well as with phase space theory.¹⁻⁴ In chemical kinetics, loose transition state theory is appropriate for reactions not having steric factors, while tight transition state theory is needed for reactions having steric effects.⁵ Phase space theory⁶ is the same as transition state theory when the transition states for both (1.1) and (1.2) are loose and when angular momentum restrictions on the latter are fully taken into account (e.g., Sec. V).

It has been suggested that the molecular beam results can be used to test the energy randomization assumption of RRKM theory,⁷ although the latter theory was designed for calculating rates^{8,9} rather than for calculating energy distributions of reactions products. When the transition states are loose, no added assumptions are indeed needed: In a loose transition state AB and C rotate freely, and so their vibrational-rotational motion is uncoupled from the radial-orbital motions in ABC^\ddagger and *a fortiori* in the motion from ABC^\ddagger to the products $AB + C$. Thus, in this case RRKM theory can be used without further approximation for discussing energy distributions.

In the case of a tight transition state, only by adding additional assumptions to it can one adapt it to yield expressions for these distributions. Thus, only when the latter assumptions are valid do the beam data test RRKM

theory itself.

In a recent stimulating theoretical study using transition state theory to obtain the energy distribution of reaction products, it was assumed that the distribution of vibrational and rotational energies in the products of (1.2) was the same as that in the transition state ABC^\ddagger .¹⁰ The translational energy distribution of relative motion of the products was assumed to be greater than that in ABC^\ddagger by a centrifugal plus potential energy term, and an appropriate distribution function for this term was included. The case of relatively large orbital angular momentum quantum numbers l in (1.2) and large ones l_0 in (1.1) was treated.¹⁰

Given the above energy distribution in ABC^\ddagger , what is of particular interest now is an examination of possible dynamical (or statistical and dynamical) effects in the evolution of the degrees of freedom of a *tight* ABC^\ddagger into those of $AB + C$. Such effects would further influence the internal and translational energy distributions of the reaction products, both for the case of large and small l . For example, some of the bending vibrational energy of ABC^\ddagger may be converted into translational energy of $AB + C$ in (1.2), as follows.¹¹

When the transition state in (1.2) is tight, there are bending vibrations in ABC^\ddagger which tend to become rotations of the products. Because the spacing of bending vibration levels is wider than that of rotational levels, an extra energy is released into translational energy E_p of the products if the conversion of the bending to rotational motion is "statistically adiabatic" (adiabatic on the average). This effect, when it occurs, would cause the translational energy of the products $AB + C$ to be shifted to higher values.

In the present paper an expression is derived for the energy distribution of the reaction products, taking this effect into account for a tight transition state. The relation between loose transition state theory and phase space theory is first summarized, so as to set a background for analysis of the tight transition state theory.

The organization of the paper is as follows. In Sec. II the transition states for some reactions are discussed, differentiating between loose and tight. In Sec. III the distribution of total angular momenta in (1.1) for a loose transition state for that reaction is given. In Sec.

IV the assumptions used in treating (1.2) are listed. State-selected cross sections are derived for the case of a loose transition state for (1.2) in Sec. V and compared with those of phase space theory. Approximations are then given for the cases of $l \gg j$ and $j \gg l$, where l and j refer to the orbital and rotational angular momenta of the products of (1.2). The corresponding cases ($l \gg j$ and $j \gg l$) when ABC^\ddagger is a tight transition state for (1.2) are treated in Sec. VI, and the former is illustrated with several examples in Sec. VII.

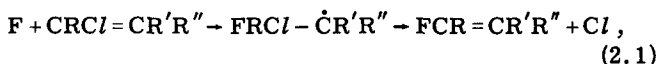
The distribution of translational energies of reaction products for the four limiting cases in Secs. V and VI is deduced in Sec. VIII from the state-selected product distributions given in those sections. Rotational and vibrational distributions are derived in Sec. IX. The paper concludes with some further comments in Sec. X.

II. TRANSITION STATES FOR SOME REACTIONS

When the reaction cross section for the forward step in (1.1) leading to the formation of an ABC^* is large, steric effects in that step are small and so the transition state of (1.1) can be regarded as loose. Because of detector sensitivity limitations the reactions studied have had relatively large cross sections and so the transition state has typically been regarded as loose for this first step.

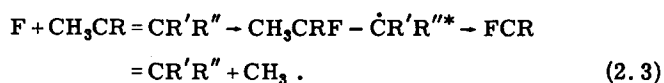
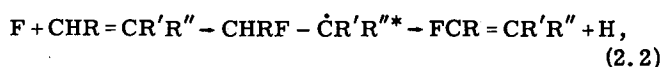
The transition state for the second step, $ABC^* \rightarrow AB + C$, Eq. (1.2), however, is probably loose for some reactions but tight for others: Typically, one might expect that when the energy barrier for the reverse step $AB + C \rightarrow ABC^*$ is large, the barrier will depend on the relative orientation of AB and C, steric effects will therefore be present and the transition state will be tight. When the barrier is negligible for the more favorable directions of mutual approach, it might be non-negligible for other directions, and some steric effects might still occur.

An example of a chemical activation whose exit channel (1.2) appears to involve no significant potential energy barrier for the reverse step, $AB + C \rightarrow ABC^*$, is



where the R's are alkyl or other groups.^{2,12a} Treatment of such reactions by a loose transition state statistical theory in which all internal coordinates of ABC^* participated in sharing the excess energy yielded reasonable agreement with the data.^{2,7}

Two other examples of chemical activation, the second of which has a large potential energy barrier^{12b,2} for the reverse step of $AB + C \rightarrow ABC^\ddagger$, involve H atom^{2,7} or methyl radical^{2,7} elimination instead of Cl elimination:



Thus, tight transition states would be expected for the dissociation step, at least in (2.3). On the basis of re-

cent beam data, one could infer either that all vibrations of ABC^* do not participate in the energy sharing during the short life of the vibrationally hot molecule,^{2,7} or that the added assumptions used to calculate the energy distribution of $AB + C$ were in error,³ or possibly both.^{3,13} The added assumptions did not, for example, allow for any possible statistical-adiabatic effect described in the previous section. The effect is such that it would qualitatively reduce the discrepancy. Thus, numerical tests of the present or other models is needed for systems involving tight transition states, before more definite conclusions can be drawn regarding the number of vibrations of ABC^* participating in the energy sharing, where ABC^\ddagger is tight.

III. DISTRIBUTION OF ANGULAR MOMENTA OF ABC^\ddagger

We consider the case where the transition state of (1.1) is loose. The final results for this aspect of problem can be altered when this step has instead a tight transition state, by utilizing arguments analogous to those employed for (1.2) in Sec. VI. All previous work appears to have used a loose transition state for (1.1).^{1,2,7,10,14}

Let l_0 and j_0 denote the orbital and the total rotational angular momentum quantum numbers for (1.1). The total angular momentum quantum number κ lies in the interval $(|l_0 - j_0|, l_0 + j_0)$, by the usual rule for addition of angular momenta.

The loose transition state occurs at the maximum of the effective potential energy for the radial motion r of AB and C: If $U_0(r)$ is the actual potential energy for motion from $r = \infty$ to an r in the vicinity of the loose transition state, the effective potential for the radial motion $B_i^0(r)$ contains a centrifugal term

$$B_i^0(r) = U_0(r) + [l_0(l_0 + 1)\hbar^2/2\mu_0 r^2]. \quad (3.1)$$

μ_0 is the reduced mass of A and BC. The transition state occurs at an r , $r_{i_0}^\ddagger$, where $B_i^0(r)$ has its maximum. (U_0 contains a long-range attractive term.) That is,

$$dB_i^0(r)/dr = 0 \quad \text{at } r = r_{i_0}^\ddagger, \quad (3.2)$$

and $d^2B_i^0(r)/dr^2$ is negative at $r_{i_0}^\ddagger$.

The reaction cross section for $A + BC$ to form initially an ABC^* in (1.1) is σ_0 . The cross section is given by a standard relation¹⁵

$$\sigma_0 = \frac{\pi}{k_0^2} \sum_{l_0=0}^{\infty} (2l_0 + 1) w_{i_0}^{l_0}, \quad (3.3)$$

where $w_{i_0}^{l_0}$ is the reaction probability for a colliding pair A and BC having an initial orbital angular momentum quantum number l_0 and an initial relative velocity v_0 . w^0 is independent of the internal states of A and BC, in the case of a loose transition state. k_0 is the wavenumber p_0/\hbar ($= \mu_0 v_0/\hbar$). w is a step function of the energy excess $E_{p_0} - B_i^0(r_{i_0}^\ddagger)$, where E_{p_0} , the initial translational energy, is $\frac{1}{2} \mu_0 v_0^2$:

$$w_{i_0}^{l_0} = 1 \quad \text{if } E_{p_0} > B_i^0(r_{i_0}^\ddagger) \\ = 0 \quad \text{if } E_{p_0} < B_i^0(r_{i_0}^\ddagger). \quad (3.4)$$

For a given E_{p_0} , therefore, w^0 is unity for all l_0 's up to some maximum value l_{om} , defined by

$$B_0^0(r_{i_0}^\dagger) < E_{p_0} \quad \text{for } l_0 < l_{om}. \quad (3.5)$$

Using (3.4) and (3.5) the sum in (3.3) now yields

$$\sigma_0 = \pi(l_{om} + 1)^2 / k_0^2. \quad (3.6)$$

Differences such as those between l_{om} and $l_{om} + 1$ will later be ignored.

The distribution of total angular momentum quantum number κ in the ABC^* 's formed in (1.1) will be needed. In the case of a loose transition state for (1.1) the probability of obtaining a particular κ for ABC^* depends only on a statistical factor: The probability of forming a particular κ in step (1.1) equals the ratio of number of κ states to total number of j_0 and l_0 states, namely, $(2\kappa + 1)/(2j_0 + 1)(2l_0 + 1)$, where κ lies in $(|j_0 - l_0|, j_0 + l_0)$. Thus, the probability that a pair $A + BC$ of a given l_0 and v_0 not only reacts but forms a state of given κ is

$$w_{v_0}^{\kappa, \kappa} = \frac{2\kappa + 1}{(2j_0 + 1)(2l_0 + 1)} w_{i_0 v_0}^0, \quad (|j_0 - l_0| \leq \kappa \leq j_0 + l_0). \quad (3.7)$$

The distribution function of ABC^* 's formed in (1.1) with a given κ , $P_0(\kappa)$, is obtained by multiplying (3.7) by the weighting factor $2l_0 + 1$, summing over all l_0 's consistent with the given κ and j_0 , and dividing by a normalizing factor:

$$P_0(\kappa) = \frac{\sum_{l_0=|\kappa-j_0|}^{\kappa+j_0} (2l_0 + 1) w_{i_0 v_0}^{\kappa, \kappa}}{\sum_{l_0=0}^{\infty} (2l_0 + 1) w_{i_0 v_0}^0}. \quad (3.8)$$

Further, $w_{i_0 v_0}^0$ equals unity when $l_0 \leq l_{om}$ and zero when $l_0 > l_{om}$, according to (3.4) and (3.5). Also, l_0 cannot exceed $\kappa + j_0$. Thus, Eqs. (3.7), (3.8), and (3.3) yield

$$P_0(\kappa) = \frac{\pi(2\kappa + 1)}{k_0^2 \sigma_0 (2j_0 + 1)} \sum_{l_0=|\kappa-j_0|}^{l_0^0} 1. \quad (3.9)$$

The upper limit l_0^0 on the l_0 sum is either the energy-limited value l_{om} defined by (3.5) or the angular momentum-limited value $\kappa + j_0$, whichever is the smaller. That is,

$$l_0^0 = \text{smaller}\{l_{om}, \kappa + j_0\}. \quad (3.10)$$

The maximum value of κ , κ_m , for the given j_0 , is the maximum value of $l_0 + j_0$, i.e.,

$$\kappa_m = l_{om} + j_0. \quad (3.11)$$

One may verify by interchanging the order of summations over κ and l_0 that¹⁶

$$\sum_{\kappa=0}^{\kappa=\kappa_m} P_0(\kappa) = 1, \quad (3.12)$$

as indeed it should. The limits in the reordered sums are given below by (3.13) since, for a given j_0 and l_0 , κ lies in the interval $(|j_0 - l_0|, j_0 + l_0)$, and since l_0 itself must lie in the interval $(0, l_{om})$:

$$|j_0 - l_0| \leq \kappa \leq j_0 + l_0, \quad 0 \leq l_0 \leq l_{om}. \quad (3.13)$$

A useful simplification of (3.9) arises, one which will not be used until Sec. VB, when $l_0 \gg j_0$. In this case,

since the l_0 's are clustered around κ , we may set in (3.9) and (3.10) (a) $|\kappa - j_0| = \kappa - j_0$ and (b) $l_0^0 = \kappa + j_0$ for the large majority of κ 's. The sum over l_0 in (3.9) then becomes $2j_0 + 1$. Further, we may set $P_0(\kappa)$ equal to zero for κ greater than l_{om} , since κ cannot exceed $l_{om} + j_0$, and this quantity is essentially l_{om} . Thus, Eqs. (3.9) and (3.6) yield

$$P_0(\kappa) = (2\kappa + 1) / l_{om}^2, \quad \kappa < l_{om} \quad (3.14a)$$

$$= 0, \quad \kappa > l_{om} \quad (3.14b)$$

ignoring the difference in l_{om}^2 and $(l_{om} + 1)^2$, for notational brevity.

IV. ASSUMPTIONS

It will be assumed that

(i) the transition state for (1.1) is loose, as already noted,

(ii) s vibrations of ABC^* participate in the energy sharing process, i.e., are active (the remaining, if any, are adiabatic throughout (1.1) and (1.2)¹⁷);

(iii) transition state theory is valid for (1.2);

(iv) in the case of a tight transition state, an additional assumption given later.

Assumption (iii) can be rephrased as

(iii) a quasiequilibrium approximation for (1.2) ("microcanonical activated complex theory"),¹⁸ namely, Eq. (4.3) below, is valid.

Assumption (i) can be replaced, as noted in the previous section; the transition state for (i) could be tight and other reaction probabilities $w_{i_0 v_0}^{\kappa, \kappa}$ could be introduced.

When the transition state ABC^\ddagger for Eq. (1.2), is loose the assumptions (i)–(iii) permit an immediate calculation of the energy distribution of the reaction products. The results are given in Sec. V, and are the same as those of phase space theory, as already noted. They reduce to those of a recently formulated loose transition state theory¹⁰ for the reaction (1.2) when one introduces the approximations, $\kappa \cong l_0$ and $l \cong \kappa$, l being the orbital angular momentum quantum number of the products. That transition state theory employed these useful approximations, and so this last result, too, is the expected one. Another limiting case, $l_0 \cong \kappa \cong j$, is also given in Sec. V.

There may be several sets of reaction products from ABC^* in reaction (1.1)–(1.2), besides $AB + C$ and $A + BC$. We denote by α the α th set of products, and introduce the following additional symbols for reaction probabilities and cross sections: $\sigma_{jn;j_0 n_0 E}^\alpha$ is the cross section for forming the α th set of products in a rotational-vibrational state jn from reactants in a state $j_0 n_0$ when the total energy is E ; $\sigma_{E_p;j_0 n_0 E}^\alpha dE_p$ is the cross section for forming the α th set of products with a translational energy $(E_p, E_p + dE_p)$; $w_{jn;l E}^{\alpha, \kappa}$ is the probability of forming an ABC^* from a collision of the α th set of products having a given j , n , l , κ , and E .

The second σ is related to the first by

$$\sigma_{E_p; j_0 n_0 E}^\alpha dE_p = \sum_{jn} \sigma_{jn; j_0 n_0 E}^\alpha, (E - E_p - dE_p \leq E_{jn}^\alpha \leq E - E_p), \quad (4.1)$$

where the sum is such that the rotational-vibrational energy E_{jn}^α of the α th set of products satisfies the condition in parentheses.

Throughout, j_0 and j denote the total rotational angular momentum of the reactants and of the α th set of products, respectively. The remaining rotational quantum numbers and the vibrational quantum numbers are included in n_0 and n , which are discussed more fully in Sec. IX.

Assumption (iii) for a given κ and E can be written as¹⁹

$$\sum_{jnl} w_{jnlE}^{\kappa\alpha} = \sum_{n^\dagger} 1 \equiv N_{\kappa\alpha}^\dagger, (|\kappa - j| \leq l \leq \kappa + j, 0 \leq E_{jn}^\alpha \leq E), \quad (4.2)$$

where the first sum is over all j , n , and l consistent with the given κ , E , and α , namely, over j , n , and l satisfying the conditions in parentheses. The sum over n^\dagger in (4.2) is over all quantum states of the ABC^\dagger for the α th set of products, consistent with the given E and κ . $N_{\kappa\alpha}^\dagger$ denotes the number of such states, apart from a degeneracy factor $2\kappa + 1$, which is absent from both sides of (4.2).

To simplify the notation the subscript α present above will be omitted in the future from all symbols, apart from $N_{\kappa\alpha}^\dagger$.

The total cross section for producing the α th set of products, $\sigma_{j_0 n_0 E}$, for the given j_0 , n_0 , and E is, in the present statistical-type theory,

$$\sigma_{j_0 n_0 E} = \sigma_0 \sum_{\kappa=0}^{\kappa_m} P_0(\kappa) \frac{N_{\kappa\alpha}^\dagger}{\sum_{\alpha} N_{\kappa\alpha}^\dagger}, \quad (4.3)$$

since $N_{\kappa\alpha}^\dagger / \sum_{\alpha} N_{\kappa\alpha}^\dagger$ is the probability that a transition state of a given κ will be of the α th type, and $\sigma_0 P_0(\kappa)$ is the contribution of a given κ to σ_0 .

When (4.2) is introduced for $N_{\kappa\alpha}^\dagger$ into the numerator of (4.3), we have

$$\begin{aligned} \sigma_{j_0 n_0 E} &\equiv \sum_{jn} \sigma_{jn; j_0 n_0 E} \\ &= \sigma_0 \sum_{\kappa=0}^{\kappa_m} \frac{P_0(\kappa)}{\sum_{\alpha} N_{\kappa\alpha}^\dagger} \sum_{jnl} w_{jnlE}^{\kappa\alpha}, \end{aligned} \quad (4.4)$$

where the conditions in (4.2) on the jnl sum apply. The sums on the right-hand side can be reordered, without any change in limits, to read $\sum_{jn} \sum_{\alpha} \sum_{l=|\kappa-j|}^{\kappa+j}$.

The right-hand side of (4.4) is now seen to be the sum of disjoint terms, since the reaction probability for $AB + C \rightarrow ABC^*$ starting from any $\kappa j n$ state of $AB + C$, $\sum_{l=|\kappa-j|}^{\kappa+j} w_{jnlE}^{\kappa\alpha}$, is independent of that starting from another $\kappa j n$ state at the same E and α . Thus, terms of the same j and n on both sides of the second half of (4.4) may be equated, yielding

$$\sigma_{jn; j_0 n_0 E} = \sigma_0 \sum_{\kappa=0}^{\kappa_m} \frac{P_0(\kappa)}{\sum_{\alpha} N_{\kappa\alpha}^\dagger} \sum_{l=|\kappa-j|}^{\kappa+j} w_{jnlE}^{\kappa\alpha}, \quad (4.5)$$

where κ_m is given by (3.11).

Assumption (iv) will be taken to be: $w_{jnlE}^{\kappa\alpha}$ is a function of the energy excess for overcoming the barrier for the reverse of (1.2), $AB + C \rightarrow ABC^*$. There is some minimum barrier, denoted by B_l^\dagger , in addition to the extra component, present statistically, from the conversion of rotations of $AB + C$ into bending vibrations of a tight ABC^\dagger . The energy excess is taken to be $E_p - B_l^\dagger$. Thus,

$$w_{jnlE}^{\kappa\alpha} = w^{\kappa}(E_p - B_l^\dagger). \quad (4.6)$$

By using microcanonical activated complex theory [assumption (iii)] one introduces an effect arising from the difference of densities of states of bending vibrations in a tight ABC^\dagger and of rotations in $AB + C$, due to the difference in energy spacing of quantum states. Assumption (iv) permits the translational energy to help overcome this mean difference in bending vibrational and rotational energy.

The simplest value for B_l^\dagger would be

$$B_l^\dagger = U^\dagger + E_l^\dagger, \quad (4.7)$$

where U^\dagger and E_l^\dagger denote the potential energy of the tight transition state ABC^\dagger , relative to the α th set of products, and a centrifugal-type barrier, respectively:

$$E_l^\dagger = l(l+1)\hbar^2/2I^\dagger. \quad (4.8)$$

Here, I^\dagger is a relevant moment of inertia of ABC . The assumption of $U^\dagger + E_l^\dagger$ as the minimal barrier provides a simple way for assuring that appropriate impact parameters for the reverse step in (1.2) occur, via a suitable I^\dagger . More complex expressions for B_l^\dagger could be tried instead. Some of the above symbols are illustrated in Fig. 1.

Equations (4.6)–(4.8) automatically apply to a loose transition state, with I^\dagger replaced by $\mu R_l^{\dagger 2}$, where R_l^\dagger is defined in Sec. V, and with w^{κ} being the simple step function given in Sec. V by Eq. (5.4). For a tight transition state the moments of inertia could depend slightly on the quantum numbers, but usually in chemical kinetics any such dependence is ignored when the transition state is tight.

The use of several additional symbols will prove helpful. We denote by l_m the upper limit of the l 's satis-

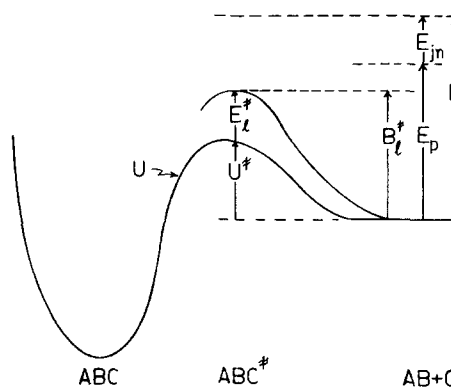


FIG. 1. Properties in the exit channel. U^\dagger may be positive, as indicated, or negative.

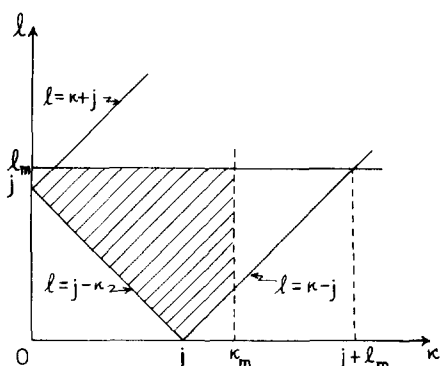


FIG. 2. Plot of (l, κ) quantum states' space available (shaded area) for forming products of a given j and E_p . The line $\kappa = \kappa_m$ is drawn for the case that $j + l_m \geq \kappa_m > j$.

fying the condition $B_l^\dagger < E_p$. That is,

$$B_l^\dagger < E_p \quad \text{for } l < l_m(E_p). \quad (4.9)$$

l_m thus depends only on E_p .

Since l can exceed neither l_m nor $\kappa + j$ and since κ can exceed neither κ_m nor $l_m + j$, Eq. (4.5) can be rewritten as

$$\sigma_{jn; j_0 n_0 E} = \sigma_0 \sum_{\kappa=0}^{\kappa_c} \frac{P_0(\kappa)}{\sum_{\alpha} N_{\kappa\alpha}^\dagger} \sum_{l=|\kappa-j|}^{l_c} w_{jnlE}^\kappa, \quad (4.10)$$

where

$$l_c = \text{smaller}\{j + \kappa, l_m\}, \quad (4.11)$$

$$\kappa_c = \text{smaller}\{j + l_m, \kappa_m\}, \quad (4.12)$$

and κ_m is given by (3.11). Thus, the upper limit of l is either an angular-momentum-limited value $j + \kappa$ or an energy-limited value l_m . Similarly, the upper limit of κ is either $j + l_m$ or κ_m , (both are energy-limited plus angular-momentum-limited values).

In two of the cases (Secs. VC and VIC) it will be convenient to interchange the order of the sums in (4.10). The new limits are seen from Fig. 2 to be

$$\sigma_{jn; j_0 n_0 E} = \sigma_0 \sum_{l=0}^{l_m} \sum_{\kappa=|j-l|}^{\kappa_c} \frac{P_0(\kappa)}{\sum_{\alpha} N_{\kappa\alpha}^\dagger} w_{jnlE}^\kappa, \quad (4.13)$$

where

$$\kappa_c' = \text{smaller}\{j + l, \kappa_m\}. \quad (4.14)$$

In Sec. VI we shall need the following densities of states of the α th set of products.

The number of active vibrational-rotational jn states of the α th products when their energy E_{jn} lies in the interval $(E - E_p - dE_p, E - E_p)$ will be denoted by $\rho(E - E_p) \times dE_p$ and equals

$$\rho(E - E_p) dE_p \equiv \sum_{jn} (2j+1), (E - E_p - dE_p \leq E_{jn} \leq E - E_p). \quad (4.15)$$

Depending on the approximation used for ρ , ρ can consist wholly of a sum of delta functions, or of delta functions (for the vibrational eigenvalues) superimposed on a continuous function, or of a continuous function.

A second density of states needed in Sec. VI involves

the sum of all n states in an energy range for systems with a given j :

$$\rho^j(E - E_p) dE_p = \sum_n 1, (E - E_p - dE_p \leq E_{jn} \leq E - E_p). \quad (4.16)$$

V. LOOSE TRANSITION STATE FOR ABC^\ddagger

A. Loose transition state for any l and j

If $U(R)$ denotes the potential energy for the radial motion R in (1.2) in the vicinity of the transition state and for larger R 's, the effective potential for the R motion $B_l(R)$ is

$$B_l(R) = U(R) + l(l+1)\hbar^2/2\mu R^2. \quad (5.1)$$

The transition state occurs at an $R = R_l^\ddagger$ where $B_l(R)$ has its maximum. R_l^\ddagger depends only on l , the orbital angular momentum quantum number of the products $AB + C$. The value of B_l at $R = R_l^\ddagger$ is denoted by B_l^\ddagger .

The quantum numbers for ABC^\ddagger are κ , j , l , and n when ABC^\ddagger is a loose transition state, and all states of this loose ABC^\ddagger are equally probable *a priori*, for the given κ and E . The total number of such states available is $\sum_{\alpha} N_{\kappa\alpha}^\dagger$, where

$$N_{\kappa\alpha}^\dagger = \sum_j \sum_n \sum_{l=|\kappa-j|}^{l_c} 1, (0 \leq E_{jn} \leq E), \quad (5.2)$$

and l_c is given by (4.11).

Since j , n , and l are good quantum numbers along the reaction coordinate R from ABC^\ddagger to $AB + C$, the distribution of j and n in $AB + C$ is the same as that in ABC^\ddagger . All states of ABC^\ddagger contributing to (5.2) are equally probable. Thus, the probability of finding a transition state in any one of these states is $1/\sum_{\alpha} N_{\kappa\alpha}^\dagger$, for the given κ and E . Since the probability of finding an ABC^* with any given κ is $P_0(\kappa)$, and since the total cross section for forming an ABC^* in (1.1) is σ_0 , the cross section for forming any j and n is obtained by summing over all l consistent with this j , κ , and n , and then summing over κ :

$$\sigma_{jn; j_0 n_0 E} = \sigma_0 \sum_{\kappa=0}^{\kappa_c} P_0(\kappa) \sum_{l=|\kappa-j|}^{l_c} \left(1/\sum_{\alpha} N_{\kappa\alpha}^\dagger\right), \quad (5.3)$$

where l_c and κ_c are given by (4.11) and (4.12).

Equations (5.3) and (3.9) are equivalent to the phase space theory result.²⁰

For later comparison we note parenthetically that the reaction probabilities w_{jnlE}^κ for the reverse of (1.2), defined in Sec. IV, is given by the following equation, in the case of a loose transition state:

$$w_{jnlE}^\kappa = 1, (E_p > B_l^\ddagger) \\ = 0, (E_p < B_l^\ddagger). \quad (5.4)$$

Equation (5.3) could also have been obtained from (4.10) using (5.4).

B. Loose transition state when $l_0 \gg j_0$ and $l \gg j$

A useful simplification of (5.3) arises when $l_0 \gg j_0$ and $l \gg j$ for the more important l_0 's and l 's contributing to

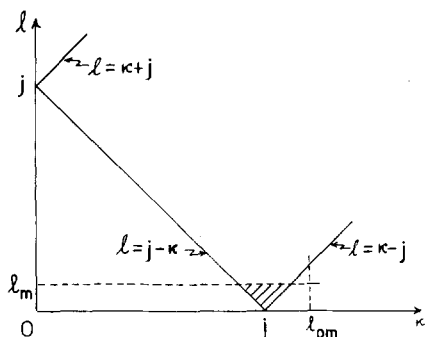


FIG. 3. Plot of (l, κ) quantum states' space available (shaded area) for forming products of a given j and E_p for the case of $j \gg l$. The line $\kappa = \kappa_m$ is drawn for the case that $\kappa_m > j + l_m$.

(5.3). It has already been seen that when $l_0 \gg j_0$, Eq. (3.9) for $P_0(\kappa)$ reduces to (3.14).

When $l \gg j$ the values of l in (5.3) are largely clustered around the given value of κ being considered. Thereby, in the sum over l in (5.3), since j is so small, we can set (a) $l_\kappa = \kappa + j$, for the large majority of the κ 's, and (b) $|\kappa - j| = \kappa - j$. Thus, the sum over l in (5.3) equals $2j + 1$.

The upper limit κ_ζ in the sum over κ in (5.3) is seen from (4.12) to be the smaller of the l_m and l_{om} , since $j + l_m \equiv l_m$ and $\kappa_m \equiv l_{om}$. Equations (5.3) and (3.14) now yield the following equation, since the sum of $2\kappa + 1$ from $\kappa = 0$ to κ_m is κ_m^2 (neglecting unity relative to κ_m):

$$\sigma_{jn;l_0 n_0 E} = \frac{(2j+1)\sigma_0}{\sum_{\alpha} N_{\kappa\alpha}^{\dagger}} A(E_p), \quad (5.5)$$

where

$$A(E_p) = 1, (l_m \geq l_{om}) \quad (5.6a)$$

$$= (l_m/l_{om})^2, (l_m \leq l_{om}). \quad (5.6b)$$

[If unity had not been neglected relative to l_m and to l_{om} , the $(l_m/l_{om})^2$ in (5.6b) would have been $(l_m+1)^2/(l_{om}+1)^2$. The same remark applies later in (5.8b).] We have replaced the κ in $\sum_{\alpha} N_{\kappa\alpha}^{\dagger}$ by some mean value, an approximation which is a convenience rather than a necessity, and have introduced a notation $A(E_p)$ to facilitate comparison with Ref. 10.²¹

C. Loose transition state when $l_0 \gg j_0$ and $j \gg l$

It will be convenient to use (4.13) for $\sigma_{jn;l_0 n_0 E}$, with $w_{\kappa n;l E}^*$ being replaced by unity for this case of a loose transition state [since $l \leq l_m$ in (4.13)]. The κ in $\sum_{\alpha} N_{\kappa\alpha}^{\dagger}$ in (4.13) will be replaced by some averaged value, and the $P_0(\kappa)$ in (4.13) is given by (3.14).

Figure 3 shows that in evaluating the sums over κ and l in (4.13) it is convenient to consider four cases which differ in the value of κ_m : (1) $\kappa_m \geq j + l_m$, (2) $j + l_m \geq \kappa_m > j$, (3) $j \geq \kappa_m > j - l_m$, and (4) $j - l_m > \kappa_m$. In the present case $j \gg l_m$ and so in practice one need consider mainly cases (1) and (4), with (2) and (3) only providing some small transition region.

For the case of $\kappa_m \geq j + l_m$ the κ'_ζ in (4.14) becomes $j + l$, the $|j - l|$ in (4.13) is $j - l$ (since $j > l$), and so in (4.13)

the sum over κ becomes a sum of $2\kappa + 1$ from $j - l$ to $j + l$. The value of this sum is $(2j+1)(2l+1)$. The sum of $2l+1$ from 0 to l_m then yields l_m^2 (neglecting unity relative to l_m).

Considering next the case $\kappa_m < j - l_m$, we note that κ cannot simultaneously satisfy the angular momentum addition rule, $j - l_m \leq \kappa \leq j + l_m$, and the condition $\kappa \leq \kappa_m < j - l_m$. Thus, the corresponding $\sigma_{jn;l_0 n_0 E}$ vanishes.

These two cases can be written as $l_{om} > j$ and $l_{om} < j$, noting that $\kappa_m \equiv l_{om}$ and $l_m < j$. Equations (4.13), (5.4), and (3.14) thus yield

$$\sigma_{jn;l_0 n_0 E} \cong \frac{(2j+1)\sigma_0}{\sum_{\alpha} N_{\kappa\alpha}^{\dagger}} A'(E_p), \quad (5.7)$$

where

$$A'(E_p) = 0 \quad \text{for } j > l_{om} \quad (5.8a)$$

$$= (l_m/l_{om})^2, \quad \text{for } j < l_{om}. \quad (5.8b)$$

Equation (5.7) plus (5.8b) is identical with the (5.5) plus (5.6b) apart from the condition $j < l_{om}$, which replaces $l_m \leq l_{om}$.

VI. TIGHT TRANSITION STATE FOR ABC[†]

A. General

Equations (4.2) and (4.6) yield

$$\sum_{jnl} w^{\kappa} = N_{\kappa\alpha}^{\dagger}, (|\kappa - j| \leq l \leq l_{\zeta}, 0 \leq E_{jn} \leq E), \quad (6.1)$$

where l_{ζ} is given by (4.12) and where w^{κ} and $N_{\kappa\alpha}^{\dagger}$ denote

$$w^{\kappa} \equiv w^{\kappa}(E_p - B_{i\kappa}^{\dagger}), \quad (6.2)$$

$$N_{\kappa\alpha}^{\dagger} \equiv N_{\kappa\alpha}^{\dagger}(E - B_{i\kappa}^{\dagger}), \quad (6.3)$$

and $B_{i\kappa}^{\dagger}$ and E_{jn}^{\dagger} are given by (4.7) and (4.8). A new quantity $B_{i\kappa}^{\dagger}$ has been introduced: $B_{i\kappa}^{\dagger}$ is the energy of ABC[†] "fixed" as potential energy U^{\dagger} and as the part of the rotational energy associated with the total angular momentum quantum number κ , and so it cannot be distributed among the states n^{\dagger} of ABC[†]. While $B_{i\kappa}^{\dagger}$ can contribute only to E_p , during the formation of the products from ABC[†], $B_{i\kappa}^{\dagger}$ can contribute both to the E_p and E_{jn} energies of the products.

When $\kappa \cong l$, the moment of inertia appearing in $B_{i\kappa}^{\dagger}$ [cf. Eq. (6.14) later] will be the same as that appearing in the exit channel barrier $B_{i\kappa}^{\dagger}$, as in case (b) below. When $\kappa \cong j$, these two moments of inertia may differ, as in case (c) below.

The summation over j, n, l is bounded by the limits in (6.1). $N_{\kappa\alpha}^{\dagger}(E - B_{i\kappa}^{\dagger})$ does not include a degeneracy factor $2\kappa + 1$, it will be recalled, which is absent from both sides. $N_{\kappa\alpha}^{\dagger}(E - B_{i\kappa}^{\dagger})$ is the number of active vibrational-rotational states of ABC[†], for given E and κ , having an internal energy equal to or less than $E - B_{i\kappa}^{\dagger}$. Equation (6.1) is to be solved for the unknown function w^{κ} .

B. Tight transition state when $l_0 \gg j_0$ and $l \gg j$

As in the corresponding case Sec. VB for the loose transition state the values of l are clustered around the value of κ . The l in $B_{i\kappa}^{\dagger}$ in (6.2) is replaced by κ . Since

$l \cong \kappa$, the moment of inertia in $B_{1\kappa}^\dagger$ is the same one as that in $B_{1\kappa}^\dagger$, and so $B_{1\kappa}^\dagger$ in (6.3) is replaced by $B_{1\kappa}^\dagger$.

The sum over l in (6.1) is from $|\kappa - j|$ to l_κ , where l_κ is, as in Sec. VB, set equal to $\kappa + j$ for almost all κ 's, because of the clustering of l values. Since $|\kappa - j|$ equals $\kappa - j$, the sum over l once again yields $2j + 1$. The sum of $2j + 1$ over j and n , for E_p in a range $(E_p, E_p + dE_p)$ yields by (4.15) $\rho(E - E_p)dE_p$, the number of rotation-vibration states for the products α in the range $E - E_p - dE_p \leq E_{jn} \leq E - E_p$. (It does not include the $2\kappa + 1$ degeneracy factor.)

Equation (6.1) then becomes

$$\int_{E_p=B_{1\kappa}^\dagger}^E \rho(E - E_p) w^\kappa(E_p - B_{1\kappa}^\dagger) dE_p = N_{\kappa\alpha}^\dagger (E - B_{1\kappa}^\dagger). \quad (6.4)$$

This equation is next solved for w^κ by Laplace transforms: Multiplying both sides of (6.4) by $\exp[-s(E - B_{1\kappa}^\dagger)]dE$, integrating from $E = B_{1\kappa}^\dagger$ to ∞ , using the convolution theorem, and noting that the Laplace transform of the right-hand side of (6.4) is $Q_\kappa^\dagger(s)/s$, where Q_κ^\dagger is defined below, we have

$$\bar{w}^\kappa(s) = Q_\kappa^\dagger(s)/sQ(s), \quad (6.5)$$

where

$$\bar{w}^\kappa(s) = \int_0^\infty w^\kappa(x) \exp(-sx) dx, \quad (6.6)$$

$$Q(s) = \int_0^\infty \rho(x) \exp(-sx) dx, \quad (6.7)$$

$$Q_\kappa^\dagger(s) = \int_0^\infty \frac{dN_{\kappa\alpha}^\dagger(x)}{dx} \exp(-sx) dx. \quad (6.8)$$

Inversion of (6.5) yields $w^\kappa(x)$. Setting x equal to $E_p - B_{1\kappa}^\dagger$ we have

$$w_{jn l E}^\kappa = w^\kappa(E_p - B_{1\kappa}^\dagger) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \frac{Q_\kappa^\dagger(s)}{sQ(s)} \exp[s(E_p - B_{1\kappa}^\dagger)] ds, \quad (6.9)$$

and with $l \cong \kappa$.

To obtain an expression for the cross section $\sigma_{jn; j_0 n_0 E}$ using (4.13), it is first noted that since $\kappa \gg j$, the values of l in the sum over l are clustered around $l = \kappa$. Setting the l in $w_{jn l E}^\kappa$ equal to some mean value κ in this small interval of l 's, the sum over l in (4.10) is from $\kappa - j$ to $\kappa + j$ and equals $(2j + 1)w_{jn l E}^\kappa$ with $l \cong \kappa$. We now have

$$\sigma_{jn; j_0 n_0 E} = (2j + 1)\sigma_0 \sum_{\kappa=0}^{\kappa_\kappa} \frac{P_0(\kappa)}{\sum_{\alpha} N_{\kappa\alpha}^\dagger} w_{jn l E}^\kappa \quad (\text{with } l \cong \kappa). \quad (6.10)$$

The upper limit κ_κ in (6.10) is seen from (4.12) to be the smaller of $j + l_m$ and κ_m , i.e., of l_m and l_{om} in this case of $l \gg j$ and $l_0 \gg j_0$. Introducing Eq. (3.14) for $P_0(\kappa)$, Eq. (6.10) thus becomes

$$\sigma_{jn; j_0 n_0 E} = (2j + 1) \frac{\sigma_0}{l_{om}^2} \sum_{\kappa=0}^{l_{om}} \frac{2\kappa + 1}{\sum_{\alpha} N_{\kappa\alpha}^\dagger} w_{jn l E}^\kappa \quad \text{for } l_m > l_{om} \quad (6.11a)$$

$$= (2j + 1) \frac{\sigma_0}{l_{om}^2} \sum_{\kappa=0}^{l_m} \frac{2\kappa + 1}{\sum_{\alpha} N_{\kappa\alpha}^\dagger} w_{jn l E}^\kappa \quad \text{for } l_m < l_{om}, \quad (6.11b)$$

where $w_{jn l E}^\kappa$ is given by (6.9).

In Eq. (6.11) the sum over κ can be replaced by an integral over $2\kappa d\kappa$, i.e., over $d(\kappa^2)$. Thus,

$$\sigma_{jn; j_0 n_0 E} = \frac{(2j + 1)\sigma_0}{\sum_{\alpha} N_{\kappa\alpha}^\dagger} A_t(E_p), \quad (6.12)$$

where the t denotes "tight" and

$$A_t(E_p) = \frac{1}{l_{om}^2} \int_{\kappa^2=0}^{l_{om}^2} w^\kappa(E_p - B_{1\kappa}^\dagger) d\kappa^2 \quad (l_m > l_{om}) \quad (6.13a)$$

$$= \frac{1}{l_{om}^2} \int_{\kappa^2=0}^{l_m^2} w^\kappa(E_p - B_{1\kappa}^\dagger) d\kappa^2 \quad (l_m < l_{om}). \quad (6.13b)$$

Here, the dependence of $\sum_{\alpha} N_{\kappa\alpha}^\dagger$ on κ has been presumed small, and the κ in $N_{\kappa\alpha}^\dagger$ represents some averaged value. (Otherwise, it can be placed in the integrand.)

From Eqs. (4.7) and (4.8), one sees that $B_{1\kappa}^\dagger$ is the sum $U^\dagger + [\kappa(\kappa + 1)\hbar^2/2I_1^\dagger]$. I_1^\dagger , it will be recalled from Sec. IV, is usually taken to be a constant in the case of a tight transition state.

Equation (6.12) also applies to a loose transition state. For a loose transition state Q_κ^\dagger equals Q in (6.9), and so (6.9) reduces²² to the step function value for w^κ given by (5.4), namely, unity if $E_p > B_{1\kappa}^\dagger$ and zero if $E_p < B_{1\kappa}^\dagger$. With this value for w^κ Eq. (6.12) yields (5.5).

C. Tight transition state when $l_0 \gg j_0$ and $j \gg l$

In this case the I^\dagger associated with the centrifugal contribution in $B_{1\kappa}^\dagger$ is expected to differ from the I^\dagger associated with the principal rotational quantum number of ABC^\dagger , κ . We shall denote the latter by I_1^\dagger , so that U^\dagger plus the part of the rotational energy of ABC^\dagger associated with κ will be denoted by $B_{1\kappa}^\dagger$, where

$$B_{1\kappa}^\dagger = U^\dagger + E_{1\kappa}^\dagger = U^\dagger + \kappa(\kappa + 1)\hbar^2/2I_1^\dagger. \quad (6.14)$$

As before, we shall suppose that E_p has to exceed a barrier $B_{1\kappa}^\dagger$, where $B_{1\kappa}^\dagger$ is given by (4.7).

In the sum over j in Eq. (6.1), the j 's are now clustered around the given value of κ . In fact, j ranges from $\kappa - l$ to $\kappa + l$, and $l \ll j$. Summing over j in this cluster and neglecting the variation in $w^\kappa(E_p - B_{1\kappa}^\dagger)$ over this j interval, the sum over j equals $2l + 1$. The sum of $2l + 1$ over l is from 0 to l_m . At any j we may, in summing over n , introduce ρ^j , the density of the states defined by (4.16). Equation (6.1) becomes

$$\int_{E_p=0}^E \rho^j(E - E_p) W^\kappa(E_p) dE_p = N_{\kappa\alpha}^\dagger (E - B_{1\kappa}^\dagger), \quad (6.15)$$

where $\kappa \cong j$ and where W^κ is defined by

$$W^\kappa(E_p) = \int_{l^2=0}^{l_m^2} w^\kappa(E_p - B_{1\kappa}^\dagger) dl^2. \quad (6.16)$$

The integrand in (6.16) depends only on E_p and $B_{1\kappa}^\dagger$. The upper limit l_m^2 depends only on E_p [cf. Eq. (4.9)]. Thus, the right-hand side of (6.16) depends only on E_p , a result explicitly indicated by the argument in $W^\kappa(E_p)$.

Equation (6.15) is solved by a Laplace transformation. Both sides are multiplied by $\exp(-sE) dE$ and integrated from $E = 0$ to ∞ . The convolution theorem yields, as in (6.4) and (6.5),

$$\bar{W}^\kappa(s) = [Q_\kappa^\dagger(s)/sQ(s)], \quad (6.17)$$

where

$$\bar{W}^*(s) = \int_0^\infty W^*(y) \exp(-sy) dy, \quad (6.18)$$

$$Q_k(s) = \int_0^\infty [dN_{\kappa\alpha}^{\dagger}(y - B_{1\kappa}^{\dagger})/dy] \exp(-sy) dy, \quad (6.19)$$

$$Q_j(s) = \int_0^\infty \rho^j(y) \exp(-sy) dy. \quad (6.20)$$

Inversion of (6.17) yields

$$W^*(y) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \frac{Q_k(s)}{s Q_j(s)} \exp(sy) ds. \quad (6.21)$$

$Q_k^{\dagger}(s)$ defined by (6.19) does not include the degeneracy $2\kappa + 1$, but the y in (6.19) does include the energy $B_{1\kappa}^{\dagger}$. The integrand in (6.19) does not become appreciable until y exceeds $B_{1\kappa}^{\dagger}$. The $\rho^j(y)$ in (6.20) is also essentially zero until y , which is E_{jn} , has some minimal value E_j for the rotational energy of the products consistent with the given j . When E_j and the rotational energy in $B_{1\kappa}^{\dagger}$ (with $\kappa \approx j$) are approximately equal, they tend to cancel in the ratio $Q_k^{\dagger}(s)/Q_j(s)$, and then W^* tends to be independent of or only weakly dependent on j .

The cross section is obtained from the reaction probability using Eq. (4.13). When l_{om} , and hence κ_m , exceeds $j + l_m$, the κ'_l in (4.13) and (4.14) is $j + l$. Since $j > l$, κ varies from $j - l$ to $j + l$. If the variation of w^* over this small κ range is neglected, the sum of $(2\kappa + 1)w^*$ from $\kappa = j - l$ to $j + l$ is $(2j + 1)(2l + 1)w^j$. Thus, Eqs. (4.13) and (3.14) yield for this case of $l_{om} > j + l_m$, i.e., of $l_{om} > j$,

$$\begin{aligned} \sigma_{jn;j_0 n_0 E} &= \frac{(2j+1)\sigma_0}{(\sum_{\alpha} N_{\kappa\alpha}^{\dagger}) l_{om}^2} \int_{l^2=0}^{l^2=l_m^2} w^j(E_p - B_l^{\dagger}) dl^2 \\ &= \frac{(2j+1)\sigma_0}{\sum_{\alpha} N_{\kappa\alpha}^{\dagger}} \frac{W^j(E_p)}{l_{om}^2}, \quad (l_{om} > j), \end{aligned} \quad (6.22)$$

where the κ in $\sum_{\alpha} N_{\kappa\alpha}^{\dagger}$ is a suitably averaged value and $W^j(E_p)$ is given by (6.21) with $\kappa \approx j$.

As in the loose case of Sec. VC, the cross section is zero when l_{om} and hence κ_m is less than $j - l_m$.

From these results we have

$$\sigma_{jn;j_0 n_0 E} = \frac{(2j+1)\sigma_0}{\sum_{\alpha} N_{\kappa\alpha}^{\dagger}} A'_t(E_p), \quad (6.23)$$

where

$$\begin{aligned} A'_t(E_p) &= 0, \quad (j > l_{om}) \\ &= \frac{1}{2\pi i l_{om}^2} \int_{c-i\infty}^{c+i\infty} \frac{Q_j^{\dagger}(s)}{s Q_j(s)} (\exp s E_p) ds, \quad (j < l_{om}). \end{aligned} \quad (6.24)$$

As in Sec. VC, the conditions $l_{om} \leq j - l_m$ and $l_{om} \geq j + l_m$ were written as $l_{om} < j$ and $l_{om} > j$, since $l_m \ll j$. The $A'_t(E_p)$ in (6.24) does not become appreciable until E_p exceeds $B_{1j}^{\dagger} - E_j$.

Equation (6.23) reduces to Eq. (5.7) for the loose transition state when the assumptions appropriate to the latter are introduced. For a loose transition state Q_j^{\dagger} can be written as

$$Q_j^{\dagger}(s) = Q_j(s) \int_0^\infty e^{-sB_l^{\dagger}} 2l dl. \quad (6.25)$$

Introduction of this result into the integral in (6.24) and integrating over s first we have²²

$$\frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \frac{Q_j^{\dagger}(s)}{s Q_j(s)} \exp(s E_p) ds = \int_0^\infty 2l dl h(E_p - B_l^{\dagger}), \quad (6.26)$$

where $h(E_p - B_l^{\dagger})$ is the unit step function, which is the same as the w_{jnlE}^* in Eq. (5.4). Thereby, h is unity if $l < l_m$ and zero if $l > l_m$ [cf. Eq. (4.9)]. The right-hand side of (6.26) thus equals $\int 2l dl$ integrated from 0 to l_m , and so equals l_m^2 . Thereby, Eq. (6.23) reduces to (5.7).

For a tight transition state the deviation of $Q_j^{\dagger}(s)/Q_j(s)$ from the value in (6.25) causes $A'_t(E_p)$ to deviate from the value (5.8) for the loose transition state.

VII. APPLICATIONS OF THE EQUATIONS IN SEC. VIB

For purposes of illustration and further discussion, Eq. (6.9) for the tight transition state $l \gg j$ is evaluated for several examples. It will be recalled that the equations of Secs. VIB and VIC applied not only to a tight transition state for assumptions made, but also to a loose transition state, when the assumptions appropriate to the latter were introduced. Equations (5.5) and (5.7) were obtained.

Since Q_k^{\dagger}/Q in (6.9) was unity for a loose transition state, the deviation of $Q_k^{\dagger}(s)/Q(s)$ from a value of unity in (6.9) represented the contribution of the steric effects to w^* for the reverse step $AB + C \rightarrow ABC^*$. (A loose transition state occurs for a reaction having no steric effects.) $Q(s)$ is known from the properties of $AB + C$. If $Q_k^{\dagger}(s)$ is calculated from the properties of the transition state and introduced into (6.9), the w^* 's can be evaluated. The various cross sections can then be calculated from (6.12). With $l \gg j$, the κ can be replaced by l in the various equations.

For concreteness, two illustrations are given below for the case where $l \gg j$ and where the transition state is tight, i.e., for the case Sec. VIB.

Example 1

We first consider an example where the high frequency vibrations contribute little (close to a factor of unity) to $Q_k^{\dagger}(s)$ and to $Q(s)$ for the s 's of interest. Their contribution to the ratio $Q_k^{\dagger}(s)/Q(s)$ is even closer to unity. We also replace, as previously noted, κ by l since $l \gg j$. If the contributions of the lower frequency motions to these partition functions are represented by

$$Q_k^{\dagger}(s) \approx A^{\dagger}/s^{m^{\dagger}}, \quad Q(s) \approx A/s^m, \quad (7.1)$$

then

$$Q_k^{\dagger}(s)/Q(s) \approx (A^{\dagger}/A) s^{m-m^{\dagger}}. \quad (7.2)$$

Equation (6.9) is then readily evaluated to yield

$$\begin{aligned} w_{jnlE}^{\dagger} &\equiv w^{\dagger}(E_p - B_l^{\dagger}) \\ &= \frac{A^{\dagger}}{A} \frac{(E_p - B_l^{\dagger})^{m^{\dagger}-m}}{\Gamma(m^{\dagger}-m+1)}, \quad (E_p > B_l^{\dagger}) \\ &= 0, \quad (E_p < B_l^{\dagger}), \end{aligned} \quad (7.3)$$

where $\Gamma(y)$ is the Γ function of the argument y . When (7.1) is a sensible approximation, the right-hand side of (7.3) will not exceed unity,²³ as indeed it should not. Equation (7.3) also reduces to Eq. (5.4) for a loose transition state, when the properties of the latter ($m^\ddagger = m, A^\ddagger = A$) are imposed.

When AB and C are a polyatomic molecule and an atom, respectively, two rotations of AB have become two bending vibrations of ABC^\ddagger , in the reverse step of (1.2). When these bending vibrations are classical each contributes unity to m^\ddagger . Each rotation contributes $\frac{1}{2}$ to m . Thus, $m^\ddagger - m$ in this case equals unity.

When AB and C are both polyatomic molecules four rotations of AB and of C have become bending vibrations, yielding a classical contribution of 2 to $m^\ddagger - m$. Of the two remaining rotations one may become a vibration or restricted rotation in the transition states contributing perhaps $\frac{1}{2}$ to $m^\ddagger - m$. The sixth rotation remains as a rotation. Thus, in this case $m^\ddagger - m$ has a value of 2–2.5.

The value of $A_t(E_p)$ is calculated from (6.13) and (7.3). If one neglects any dependence of I^\ddagger and U^\ddagger on l , as one typically does in the case of a tight transition state but not in the case of a loose one, Eqs. (6.13) and (7.3) yield,²⁴ noting that $\kappa \cong l$,

$$A_t(E_p) = \frac{A^\ddagger}{A} \left(\frac{l_m^2 \hbar^2}{2I^\ddagger} \right)^{m^\ddagger - m} \left(\frac{l_m}{l_{om}} \right)^2 \times \frac{1 - [1 - (l_{om}/l_m)^2]^{m^\ddagger - m + 1}}{\Gamma(m^\ddagger - m + 2)}, \quad (l_m > l_{om}) \quad (7.4a)$$

$$= \frac{A^\ddagger}{A} \left(\frac{l_m^2 \hbar^2}{2I^\ddagger} \right)^{m^\ddagger - m} \left(\frac{l_m/l_{om}}{\Gamma(m^\ddagger - m + 2)} \right)^2, \quad (l_m < l_{om}). \quad (7.4b)$$

Although (7.4) was explicitly derived for a tight transition state it also reduces to $A(E_p)$, given by (5.6), for a loose one.²⁵

Example 2

For a second example we shall suppose that there is much cancellation of Q_r^\ddagger and Q in (6.9), apart from those contributions which are bending vibrations in ABC^\ddagger and rotations in $AB+C$. Let the number of these rotations be m_r . The rotations can be treated as classical. We let their contribution to $Q(s)$ be $Q_r(s)$, and write

$$Q_r(s) = A_r / s^{m_r/2}, \quad (7.5)$$

since each rotation contributes \sqrt{s} to $s^{m_r/2}$. The contribution of the bending vibrations to $Q_r^\ddagger(s)$ is denoted by $Q_b^\ddagger(s)$. Equation (6.9) now becomes, with $\kappa \cong l$,

$$w^i(E_p - B_i^\ddagger) = \frac{1}{2\pi i A_r} \int_{c-i\infty}^{c+i\infty} s^{(m_r/2)-1} \times Q_b^\ddagger(s) \exp[s(E_p - B_i^\ddagger)] ds \quad (7.6)$$

i. e.,

$$= \frac{1}{A_r} \frac{d^{m_r/2}}{dE_p^{m_r/2}} N_r^\ddagger(E_p - B_i^\ddagger), \quad (7.7)$$

Eq. (7.7) applying to the case that m_r is an even integer. When AB is a linear molecule and C is an atom m_r is 2. When AB and C are both polyatomic molecules and when

the four of the six rotations become bending vibrations while the other two remain as rotations, m_r is 4. N_r^\ddagger can be evaluated by a direct counting technique as well as by more approximate methods.^{9,26} When m_r is an odd integer (7.6) can be evaluated by a variety of methods. For example, $s^{-1/2} Q_r^\ddagger(s)$ can be treated as a product of partition functions, the $s^{-1/2}$ being, apart from a proportionality constant, the partition function of a plane rotor. The corresponding "number of states" function will be denoted by $N_r^\ddagger(E_p - B_i^\ddagger)$. The latter could be evaluated by direct counting or by approximate methods. Equation (7.6) then applies, with N^\ddagger replaced by N_r^\ddagger and with $m_r/2$ replaced by $m_r + \frac{1}{2}$, an even integer.

For the model in this example, $A_t(E_p)$ is obtained from (6.13) and (7.7). For the case where $m_r/2$ is an integer we have, for a tight transition state,

$$A_t(E_p) = \frac{1}{A_r \mathcal{E}_{om}^2} \frac{dN_r^\ddagger M_r^{-1} (\mathcal{E}_m^2 - \mathcal{E}^2)}{d(-\mathcal{E}^2)^{(M_r-1)}} \Big|_{\mathcal{E}=\mathcal{E}_{om}}^{\mathcal{E}=0} \quad (l_m > l_{om}) \quad (7.8a)$$

$$= \frac{1}{A_r \mathcal{E}_{om}^2} \frac{dN_r^\ddagger M_r^{-1} (\mathcal{E}_m^2 - \mathcal{E}^2)}{d(-\mathcal{E}^2)^{(M_r-1)}} \Big|_{\mathcal{E}=\mathcal{E}_m}^{\mathcal{E}=\mathcal{E}_{om}} \quad (l_m < l_{om}), \quad (7.8b)$$

where the right-hand side indicates a difference of the values derivative at the upper and lower limits, and where

$$\mathcal{E}^2 = l^2 \hbar^2 / 2I^\ddagger, \quad M_r = m_r / 2. \quad (7.9)$$

\mathcal{E}_{om} is given by (7.9) with l replaced by l_{om} .

VIII. TRANSLATIONAL ENERGY DISTRIBUTION OF REACTION PRODUCTS

We shall consider the cases of Secs. VB, VC, VIB, and VIC in that order. In all cases Eq. (4.1) is used to relate $\sigma_{E_p; i j 0 n 0 E}$ to $\sigma_{j n; i j 0 n 0 E}$.

(i) Case of Sec. VB (loose transition state, $l \gg j$)

Equation (5.5) is introduced into (4.1), noting that $A(E_p)$ does not depend on j or n , for a given E_p . The sum $\sum_{j,n} (2j+1)$ over the energy range $E - E_p - dE_p \leq E_{jn} - E_p$ is the number of vibrational-rotational states, $\rho(E - E_p) dE_p$, given by (4.15) for the α th set of products. Equations (4.1) and (5.5) then yield

$$\sigma_{E_p; i j 0 n 0 E} = \frac{\sigma_0}{\sum_{\alpha} N_{\alpha}^\ddagger} \rho(E - E_p) A(E_p), \quad (8.1)$$

where $A(E_p)$ is given by (5.6). l_m depends only on E_p ; l_{om} depends only on E_{p0} .

Equations (8.1) is equivalent to that derived by Safron *et al.*^{10,27} Thus, the latter equation yields the same result as phase space theory for the (highly useful) simplifying assumptions of $l \gg j$ and $l_0 \gg j_0$. The latter assumptions were explicitly made in Ref. 10.

(ii) Case of Sec. VC (loose transition state $j \gg l$)

In Eq. (5.7), $A'(E_p)$ depends only on E_p , for a given E_{p0} since l_m in (5.8) depends only on E_p . Summing (5.7) over j and n in the energy range $(E - E_p - dE_p \leq E_{jn} \leq E - E_p)$ yields the sum $\sum_{j,n} (2j+1)$, which can again be written as $\rho(E - E_p) dE_p$. Equation (5.7) then yields

$$\sigma_{E_p; j_0 n_0 E} = \frac{\sigma_0}{\sum_{\alpha} N_{\kappa \alpha}^{\dagger}} \rho(E - E_p) A'(E_p), \quad (8.2)$$

where $A'(E_p)$ is given by (5.8).

(iii) Case of Sec. VIB (tight transition state, $l \gg j$)

In Eq. (6.12), $A_t(E_p)$ depends only on E_p . On summing (6.12) over j and n in the energy range $E - E_p - dE_p \leq E_{jn} \leq E - E_p$, one obtains $\sum_{jn} (2j+1)$, i.e., the $\rho(E - E_p) dE_p$ in (4.15). Equations (4.1) and (6.12) yield

$$\sigma_{E_p; j_0 n_0 E} = \frac{\sigma_0}{\sum_{\alpha} N_{\kappa \alpha}^{\dagger}} \rho(E - E_p) A_t(E_p), \quad (8.3)$$

where $A_t(E_p)$ is given by (6.13).

(iv) Case of Sec. VIC (tight transition state $j \gg l$)

When the j dependence of $Q_j^{\dagger}(s)/Q_j(s)$ in (6.24) is weak, for the reason discussed in Sec. VI, the dependence of $A_t'(E_p)$ on j there is weak also. The summation of (6.23) over j and n in the energy interval $E - E_p - dE_p \leq E_{jn} \leq E - E_p$ yields $\sum_{jn} (2j+1)$, which is again the $\rho(E - E_p) dE_p$ in (4.15). Equations (4.1) and (6.23) then yield

$$\sigma_{E_p; j_0 n_0 E} = \frac{\sigma_0}{\sum_{\alpha} N_{\kappa \alpha}^{\dagger}} \rho(E - E_p) A_t'(E_p), \quad (8.4)$$

where $A_t'(E_p)$ is given by (6.24).

IX. ROTATIONAL AND VIBRATIONAL ENERGY DISTRIBUTION OF REACTION PRODUCTS

It is useful to first describe more fully in Eq. (9.1) below the quantum number n appearing in Secs. III–VIII. (Similar remarks apply to n_0 .) The collision pair in the reverse of step (1.2) is specified by the quantum numbers j , n , l (and by the momentum p). The quantum numbers for a pair of molecules 1 and 2 in an uncoupled basis would be j_1 , m_{j_1} , k_1 , j_2 , m_{j_2} , k_2 , l , m_l , and v , where v denotes the vibrational quantum numbers for all vibrational degrees of freedom of both molecules, j_1 and j_2 denote the rotational angular momentum quantum numbers of the molecules, m_{j_1} and m_{j_2} the z components, and k_1 and k_2 are the extra rotational quantum numbers needed to specify the eigenvalues if the molecules are nonlinear. For example, k_1 is absent when molecule 1 is linear, and j_1 and m_{j_1} are absent²⁸ if molecule 1 is an atom. In a coupled basis, the quantum numbers are j , l , κ , m_{κ} , and j_1 , k_1 , j_2 , k_2 , v , the same number of them as before, of course. m_{κ} has already been included by the $2\kappa+1$ factor present in Eq. (3.9) for $P_0(\kappa)$. Thus, the quantum number n denotes

$$n \equiv \{j_1, k_1, j_2, k_2, v\}, \quad (9.1)$$

of which some of these may be absent if one of the product molecules is an atom or a linear molecule.

Thus, if the distribution of only certain of the quantum numbers of molecule 1, n_1 say, is measured, the relevant cross section describing the distribution is

$$\sigma_{n_1; j_0 n_0 E} = \sum_{(m \neq n_1)} \sum_{j_1+j_2}^{j_1+j_2} \sigma_{j_1 j_2; j_0 n_0 E}, \quad (9.2)$$

where the notation is intended to indicate that the summation over n is made at fixed n_1 .

Regardless of whether 1 or 2 are linear or nonlinear, or whether 2 is an atom, the only dependence of $\sigma_{j_1 j_2; j_0 n_0 E}$ on j lies in the $2j+1$ factor in the case of cases of Secs. VB and VIB. In VC the only other dependence on j is in the existence of a cutoff for $j > l_{om}$ [Eq. (5.8)]. In Sec. VIC there is a similar cutoff in (6.24), and an additional weak j dependence.

We consider cases of Secs. VB and VIB first. Here, the sum over j in (9.2), using (5.5) or (6.12), involves a sum of $2j+1$ from $j = |j_1 - j_2|$ to $j_1 + j_2$. This sum equals $(2j_1+1)(2j_2+1)$. In the subsequent sum in (9.2) over n at fixed n_1 we note that $A(E_p)$ in Eq. (5.5) and $A_t(E_p)$ in Eq. (6.12) for $\sigma_{j_1 j_2; j_0 n_0 E}$ do not depend on n for a given E_p . The sum of $2j_2+1$ over j_2 and the other contributors to n is next written as the sum (integral) of contributions from various dE_p intervals. The contribution to this n sum from the E_{jn} 's in the range indicated in (9.3), at the given n_1 , is denoted by $\rho^{(n_1)}(E - E_p) dE_p$. That is,

$$\sum_{(n \neq n_1)} (2j_1+1)(2j_2+1) = \rho^{(n_1)}(E - E_{n_1} - E_p) dE_p, \quad (E - E_p - dE_p \leq E_{jn} \leq E - E_p), \quad (9.3)$$

where E_{n_1} is the energy of the degrees of freedom contributing to the specified n_1 and $E - E_{n_1} - E_p$ is the energy distributed among the remaining rotations and vibrations of AB and C.

Equations (9.2), (9.3), and (5.5) or (6.12) yield

$$\sigma_{n_1; j_0 n_0 E} = \frac{\sigma_0}{\sum_{\alpha} N_{\kappa \alpha}^{\dagger}} \int_{E_p=0}^{E-E_{n_1}} \rho^{(n_1)}(E - E_{n_1} - E_p) C(E_p) dE_p, \quad (9.4)$$

where

$$C(E_p) = A(E_p) \quad (\text{Sec. VB}) \quad (9.5)$$

$$= A_t(E_p) \quad (\text{Sec. VIB}), \quad (9.6)$$

and $A(E_p)$ and $A_t(E_p)$ are given by (5.6) and (6.13), respectively.

When $j_1 \gg j_2$, so that the condition $j > l_{om}$ or $< l_{om}$ in (5.8) and (6.24) becomes $j_1 > l_{om}$ or $< l_{om}$, and so does not depend on j_2 , and when j_1 is one of the n_1 's, (9.4) applies to the other cases (in the case of Sec. VIC if the cited weak j dependence is neglected), but now

$$C(E_p) = A'(E_p) \quad (\text{Sec. VC}) \quad (9.7)$$

$$= A_t'(E_p) \quad (\text{Sec. VIC}), \quad (9.8)$$

where A' and A_t' are given by (5.8) and (6.24), respectively, with j replaced by j_1 .

To illustrate (9.3) and (9.4), we note that if molecule 1 is a diatomic molecule and molecule 2 is an atom, and if n_1 denotes j_1 and v_1 , the vibrational quantum number of molecule 1, $\rho^{(n_1)}(E - E_p - E_{n_1})$ equals $(2j_1+1) \delta(E - E_{j_1} - E_{v_1} - E_p)$ and Eq. (9.4) with $j_1 \equiv j$ reduces to (5.5), (5.7), (6.12), or (6.23), depending on the case being studied.

If, instead, in this last example n_1 denotes only j_1 ,

$\rho^{(n_1)}(E - E_p - E_{n_1})$ equals $(2j_1 + 1)$ times the density of vibrational states of molecule 1, $\rho^v(E - E_p - E_{j_1})$. Or again, if molecule 1 is a linear molecule and if molecule 2 is linear or nonlinear, and if n_1 denotes the rotational-vibrational state ($j_1 v_1$) of molecule 1, $\rho^{(n_1)}(E - E_p - E_{n_1})$ equals $(2j_1 + 1)$ times the degeneracy, if any, associated with v_1 , and times the density of rotational-vibrational states of molecule 2. If, in this last example, n_1 denotes only j_1 , $\rho^{(n_1)}(E - E_p - E_{n_1})$ is the convolution of the vibrational state density of molecule 1 and the rotational-vibrational state density of molecule 2.

X. CONCLUDING DISCUSSION

Expressions for the various state-selected and energy distributions of products are given in Secs. V-IX. The distributions are seen to depend on the relevant degeneracies or densities of the active modes¹⁷ of the reaction products AB+C and on the reaction probabilities for the reverse step in (1.2), AB+C \rightarrow ABC*. This result is expected, because of the assumption regarding the role of active modes in ABC* and because of microscopic reversibility. Assumption (iv) makes a particular assumption about these reaction probabilities, and, in conjunction with assumption (iii) yields an expression for them.

There is a considerable indirect body of data on the behavior of state-selected reaction probabilities for the case of direct reactions. However, little is known yet about those probabilities for reactions which may proceed via transient species, and there could be substantial differences.²⁹

The expressions for loose and tight transition states have in common the presence of degeneracy or state density factors for the active modes, e.g., for the case of $l \gg j$, they have in Eqs. (8.1) and (8.3) $\rho(E - E_p)$ with $\rho(E - E_p)$ defined in (4.15). They differ in the reaction probabilities for the reverse step of (1.2), and so $A(E_p)$ in the former [Eq. (8.1)] is replaced by $A_t(E_p)$ in the latter [Eq. (8.3)]. Comparison of $A(E_p)$ with $A_t(E_p)$ shows that at higher E_p 's (where $l_m > l_{om}$ in exothermic reactions) $A_t(E_p)$ results in a predicted shift in E_p distribution toward higher E_p 's, compared with $A(E_p)$ [cf. (5.6a) with (6.13a)]. The origin of this predicted shift is discussed in Sec. I.

We have already noted that translational energy distribution of products of the loose transition state for the case of $l \gg j$ was treated earlier¹⁰ and that the present result [Eqs. (8.1) and (5.6)] agrees with that in Ref. 10. The case of a tight transition state was also discussed in Ref. 10 for the case of $l \gg j$, using a different model for the exit channel behavior. They assumed that the translational energy E_p in the products of (1.2) was the same as that in ABC*, plus an amount B_t^\ddagger . In the present paper we assume that some conversion of bending vibrational to translational energy can occur, resulting in the tight transition state case (Sec. VIB) in E_p being larger than the sum of the translational energy in ABC* plus B_t^\ddagger .

It is useful to compare the two results by considering an approximate model such as that involved in Sec. VII,

Example 1. However, we shall take all coordinates to be classical now, for purposes of the illustration. Each vibration in ABC* (apart from the adiabatic ones¹⁷) contributes 1 to the m^\ddagger in the classical expression (7.1). Each active rotation in ABC* contributes $\frac{1}{2}$. Thus, the value of m^\ddagger is

$$m^\ddagger = s^\ddagger + \frac{1}{2}r, \quad (10.1)$$

where r is the number of "nonadiabatic" rotations in ABC* and s^\ddagger is the number of active vibrations in ABC*.^{30,31}

The expression in Ref. 10 for the relative translational energy distribution is³⁰

$$\begin{aligned} \sigma_{E_p; j_0 n_0 E} &= \text{const. } (E - E_p)^{r/2 + s^\ddagger - 1}, \quad l_m \geq l_{om} \quad (10.2a) \\ &= \text{const. } (l_m/l_{om})^2 (E - E_p)^{r/2 + s^\ddagger - 1}, \quad l_m < l_{om}. \end{aligned} \quad (10.2b)$$

The dependence of l_m on E_p when a potential $-c/r^n$ is used for U is given in Ref. 10.

For a loose transition state the density of states of the products $\rho(E - E_p)$ in (8.1) is the same as that for these coordinates in ABC*, namely, $\text{const. } (E - E_p)^{r/2 + s^\ddagger - 1}$. Thus, Eq. (8.1) in this case is the same as Eq. (10.2), which was taken from Ref. 10.

For a tight transition state Eq. (8.3) gives

$$\sigma_{E_p; j_0 n_0 E} = \text{const. } A_t(E_p)(E - E_p)^{m-1}, \quad (10.3)$$

where

$$m = r_p/2 + s_p. \quad (10.4)$$

The p subscript refers to products, r_p being the number of active rotations of the products and s_p the number of their active vibrations. [For a loose transition state $r_p = r$ and $s_p = s^\ddagger$.] In (10.3) $A_t(E_p)$ is given by (7.4). At high enough translational energies where $l_{om} \ll l_m$, the latter equation for $A_t(E_p)$ yields

$$A_t(E_p) \cong \text{const. } l_m^{2(m^\ddagger - m)}, \quad (l_m \gg l_{om}). \quad (10.5)$$

For the model used in Ref. 10, l_m^2 is roughly proportional to E_p . For this case one would then write

$$\sigma_{E_p; j_0 n_0 E} \cong \text{const. } E_p^{m^\ddagger - m} (E - E_p)^{m-1}, \quad (l_m \gg l_{om}), \quad (10.6)$$

which compares with (10.2a), i.e., with

$$\sigma_{E_p; j_0 n_0 E} \cong \text{const. } (E - E_p)^{m^\ddagger - 1}, \quad (l_m > l_{om}). \quad (10.7)$$

For a tight transition state, m^\ddagger is larger than m by an amount equal to one-half the number of bending vibrations which have become rotations.³² Thus, both because the factor $E_p^{(m^\ddagger - m)}$ in (10.6) increases with E_p and because the factor $(E - E_p)^{m-1}$ decreases less rapidly with increasing E_p than does $(E - E_p)^{m^\ddagger - 1}$, the E_p distribution predicted by (10.6) is shifted toward higher E_p 's, in the case of a tight transition state, than that predicted by the Eq. (10.7) based on Ref. 10. The physical explanation was given earlier in Sec. I.

ACKNOWLEDGMENT

I am indebted to Gary Worry for his comments.

- *Research supported by the Explosives Division, Feltman Research Laboratories, Picatinny Arsenal, Dover, N.J.
- ¹See review by D. R. Herschbach, *Faraday Discuss. Chem. Soc.* 55, 233 (1973); cf. D. L. King and D. R. Herschbach, *ibid.* 55, 331 (1974); S. J. Riley and D. R. Herschbach, *J. Chem. Phys.* 58, 27 (1973).
- ²See the review by Y. T. Lee, *Ber. Bunsenges Phys. Chem.* 78, 135 (1974); Y. T. Lee, in *Proceedings of the XI International Symposium on Free Radicals* (Munich, West Germany, 1973); J. M. Farrar and Y. T. Lee, *Ann. Rev. Phys. Chem.* 25, 357 (1974).
- ³J. G. Moehlmann, J. T. Gleaves, J. W. Hudgens, and J. D. McDonald, *J. Chem. Phys.* 60, 4790 (1974).
- ⁴P. J. Dagdigan, H. W. Cruse, A. Schultz, and R. N. Zare, *J. Chem. Phys.* 61, 4450 (1974).
- ⁵For example, R. A. Marcus and O. K. Rice, *J. Phys. Colloid Chem.* 55, 894 (1951), where the transition states were termed loose and rigid. Following the terminology in Ref. 1, the latter will now be called tight.
- ⁶P. Pechukas and J. C. Light, *J. Chem. Phys.* 42, 3281 (1965); P. Pechukas, J. C. Light, and C. Rankin, *ibid.* 44, 794 (1966).
- ⁷J. M. Parson, K. Shobatake, Y. T. Lee, and S. A. Rice, *J. Chem. Phys.* 59, 1402 (1972); K. Shobatake, J. M. Parson, Y. T. Lee, and S. A. Rice, *ibid.* 59, 1416 (1973); 59, 1427 (1973); K. Shobatake, Y. T. Lee and S. A. Rice, *ibid.* 59, 1435 (1973); J. M. Parson, K. Shobatake, Y. T. Lee, and S. A. Rice, *Faraday Discuss. Chem. Soc.* 55, 344 (1973); J. M. Parson and Y. T. Lee, *J. Chem. Phys.* 56, 4658 (1972).
- ⁸Compare Ref. 5; R. A. Marcus, *J. Chem. Phys.* 20, 359 (1952); 43, 2658 (1965); 52, 1018 (1970).
- ⁹P. J. Robinson and K. A. Holbrook, *Unimolecular Reactions* (Wiley, New York, 1972); W. Forst, *Theory of Unimolecular Reactions* (Academic, New York, 1973); L. D. Spicer and B. S. Rabinovitch, *Ann. Rev. Phys. Chem.* 21, 349 (1970).
- ¹⁰S. A. Safron, N. D. Weinstein, and D. R. Herschbach, *Chem. Phys. Lett.* 12, 564 (1972); cf. W. B. Miller, S. A. Safron, and D. R. Herschbach, *Discuss. Faraday Soc.* 44, 108 (1967).
- ¹¹R. A. Marcus, *J. Chem. Phys.* 45, 2630 (1966); 46, 959 (1967).
- ¹²(a) The activation energy for halide + olefin is about 1 kcal/mole [J. Knox and K. C. Waugh, *Trans. Faraday Soc.* 65, 1585 (1969); P. B. Ayscough, A. J. Cocker, F. S. Dainton, and S. Hirst, *ibid.* 58, 318 (1962)]. (b) The activation energy for CH_3 + olefin is about 8 kcal/mole [cf. R. J. Cvetanovic and R. S. Irwin, *J. Chem. Phys.* 46, 1694 (1967); A. M. Hogg and P. Kebarle, *J. Am. Chem. Soc.* 86, 4558 (1964)] and that for H + olefin is about 3 kcal/mole [K. Yang, *ibid.* 84, 3795 (1962); J. H. Knox and D. G. Dalgleish, *Int. J. Chem. Kinet.* 1, 69 (1969); W. E. Jones, S. D. Macknight, and L. Teng, *Chem. Revs.* 73, 407 (1973)]. None of the systems in (a) or (b) referred explicitly to the addition of these atoms or radical to fluoro-olefins. The presence of an F on a carbon atom to which the H is adding reduces the rate by a factor of ~ 5 –15 [cf. data of J. P. Kilcoyne and K. R. Jennings, *J. Chem. Soc. Faraday I* 70, 379 (1974); I am indebted to Professor B. S. Rabinovitch for referring me to this article]. Correspondingly, the activation energy could be 1–1.5 kcal/mole higher.
- ¹³R. A. Marcus, *Faraday Discuss. Chem. Soc.* 55, 379 (1974); 55, 381 (1974); cf. discussion comments by several investigators on pp. 376–380 of this journal.
- ¹⁴Phase space theory for (1.1) implies the assumption of a loose transition state for that step.
- ¹⁵For example, L. D. Landau and E. M. Lifschitz, *Quantum Mechanics* (Addison-Wesley, Reading, Mass., 1958), p. 437. Classically, it will be recalled that (3.3) represents the contribution to σ from the area element $2\pi b db$ times the reaction probability $w^0(b)$, from impact parameters in the range $(b, b + db)$, and integrated from $b = 0$ to $b = \infty$. Substitution of the semiclassical relation $(l + \frac{1}{2})\hbar = \text{orbital angular momentum} = b p_0$, yields the integral counterpart of (3.3), $\pi \int_0^\infty (2l + 1) dl w^0(b)/k_0^2$, where $k_0 = p_0/\hbar$.
- ¹⁶Using the limits in (3.13), the sum of $2\kappa + 1$ in the $P_0(\kappa)$ in (3.9) is from $\kappa = |j_0 - l_0|$ to $j_0 + l_0$ and equals $(2l_0 + 1)(2j_0 + 1)$. When $(\pi/k_0^2 \sigma_0)(2l_0 + 1)$ is then summed over l_0 using the limits in (3.13) and using the σ_0 given by (3.3) and (3.4), the result is unity.
- ¹⁷The quantum number for an adiabatic degree of freedom remains constant during the process. Its energy may vary somewhat, since its energy depends not only on its quantum number but also on molecular properties such as its vibration frequency, anharmonicity, if any, etc. The energy of the adiabatic vibrations can be treated as being included in a potential energy function for the remaining coordinates. We shall suppose that this convenient device has been used. If all vibrations are active, i.e., if no vibrations are adiabatic, s equals the number of vibrations of ABC*. For a sufficiently short-lived ABC* some of these vibrations may not be active.
- ¹⁸R. A. Marcus, *J. Chem. Phys.* 45, 2138 (1966).
- ¹⁹Ref. 18, Eq. (6), apart from a number of notational differences: The n there includes the n and j here; n^\dagger denotes n^\ddagger ; j denotes κ ; a transmission coefficient denoted there by κ is set equal to unity here, since we are considering a classical case in the present paper. Adiabatic degrees of freedom there were denoted by v .
- ²⁰The phase space theory result for three and four atom systems are given in Refs. 6 and 4, respectively, and summarized in Ref. 4. To relate Eqs. (3.9) plus (5.3) to Eqs. (A1) and (A3) of Ref. 4 the order of summation over l_0 and κ in the former is interchanged, the new limits being given by (3.13).
- ²¹However, throughout, the primed and unprimed quantities in Ref. 10 refer to products and reactants, respectively, whereas we use unprimed and zero-subscripted quantities for the same purpose. Further, the subscript t in Ref. 10 is the same as the present subscript p .
- ²²A. Erdelyi, *Tables of Integral Transforms* (McGraw-Hill, New York, 1964), Vol. 1, p. 133.
- ²³ Q_κ^\ddagger/Q is unity for a loose transition state but less than unity for a tight one. One sees from (7.3) that the $1/s$'s of interest in (7.2) are of the order of $E_p - B_t^\ddagger$. Thus, Eq. (7.2) and the condition that $Q_\kappa^\ddagger/Q \leq 1$ implies that the right-hand side of (7.3) does not exceed unity, as long as (7.1) is a reasonable approximation.
- ²⁴The fact that $E_p - U^\ddagger$ equals $l_m^2 \hbar^2 / 2I^\ddagger$ was used.
- ²⁵This paradox is explained by the fact that (7.3) is valid for both loose and tight transition states, and the integral (6.13) is trivial for a loose transition state, so that the assumption that I^\ddagger and U^\ddagger in (7.4) are l independent causes no error even when the transition state is loose.
- ²⁶S. E. Stein and B. S. Rabinovitch, *J. Chem. Phys.* 58, 2438 (1973), and references cited therein.
- ²⁷Compare with Eq. (1) of Ref. 10, where $A(E_f^\ddagger)$ is the same as $A(E_p)$. The $N_m^\ddagger(E' - E_f^\ddagger)$ is the same as our $\rho(E - E_p)$, since the internal degrees of freedom in a loose transition state are the same as those of the reaction products.
- ²⁸Electronic angular momenta make a negligible contribution and have been ignored throughout. Any statistical factors to which they may contribute can be included at the appropriate places.
- ²⁹In direct collisions, the potential energy surfaces of exothermic reactions are characterized by the terms "early downhill," "late downhill," as well as some intermediate category [cf. reviews by T. Carrington and J. C. Polanyi and by J. L. Kinsey, in *MTP International Review of Science, Phys. Chem. Ser. I, Vol. IX. Chemical Kinetics*, edited by J. C. Polanyi (Butterworths, London, 1972), Chaps. 5 and 6, respectively]. The early downhill type refers to the case where the major decrease in potential energy along the reaction coordinate occurs before the region where the coordinate is highly curved in the usual skewed axis diagram. Late downhill refers to the case where the large decrease in potential energy occurs mainly after the system has passed through this

curved region. The early downhill yields highly vibrationally excited reaction products, while the late downhill one causes translationally excited products. However, in the case of a three atom $A + BC \rightarrow AB + C$ reaction, this curved region is occupied by the ABC^* . Thus, if an energy randomization occurs within an ABC^* molecule the above considerations do not apply. When an energy randomization does not occur they do apply although in diluted form if there is some randomization. In either case, a knowledge of the nature of the potential energy surface from the ABC^* region to the $AB + C$ region would be useful.

³⁰This number is not to be confused with that of ABC^* . When the transition state ABC^\ddagger is tight, s^\ddagger is one less than the number of active vibrations of ABC^* , because one of the active vibrations in ABC^* has become the reaction coordinate in ABC^\ddagger . When the transition state is loose s^\ddagger is more than one

less than the number of active vibrations in ABC^* , because some of those vibrations have become rotations.

³¹Cf. Eqs. (1), (8), and (12) of Ref. 10. The quantity denoted by $s - 1$ in Ref. 10 is the same as our s^\ddagger , since they include in their s the reaction coordinate, whereas s^\ddagger does not. Other notational differences are noted in Ref. 27 of the present paper.

³²The total number of degrees of freedom of ABC^\ddagger in the center of mass system of coordinates is $r + s^\ddagger + 3$, since in addition to the $r + s^\ddagger$ there are two adiabatic rotations and one reaction coordinate. The total number of degrees of freedom of $AB + C$ in the center of mass system of coordinates is $r_p + s_p + 3$, since in addition to the $r_p + s_p$ there are two orbital plus one radial degrees of freedom. Thus, $r + s^\ddagger$ equals $r_p + s_p$. But $m^\ddagger - m$ is, by (10.1) and (10.4), therefore equal to $(s^\ddagger - s_p)/2$.