Reprinted from The Journal of Chemical Physics, Vol. 45, No. 7, 2630–2638, 1 October 1966
Printed in U. S. A.

On the Theory of Chemical-Reaction Cross Sections. I. A Statistical-Dynamical Model*

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(Received 14 March 1966)

A statistical-dynamical model is formulated for total chemical-reaction cross sections as a function of the relative velocity and the vibrational and the rotational state of the reactants. It is derived for reactions for which activated-complex configurations can be defined; reactions with or without steric and activation barriers. A quasiequilibrium is postulated between reacting pairs and activated complexes of the same energy and angular momentum. An integral equation is obtained which is solved for the reaction cross section by introduction of a second postulate: The reaction probability is a function of the excess initial energy along the reaction coordinate (in excess of potential energy barrier, centrifugal potential barrier, and vibrational adiabatic requirements). A possible dynamical origin of the postulates is considered in later papers.

I. INTRODUCTION

With the advent of molecular-beam studies of chemical reactions, increasing attention has been focused on differential and total reaction cross sections. At least three theoretical approaches to such problems can be envisaged, in decreasing order of rigor but in increasing order of simplicity: (1) exact numerical integration of the classical or quantum-mechanical equations of motion of the atoms in the reactive collision, (2) approximate analytic integration of such equations using approaches related to some employed in the study of physical elastic and inelastic collisions, and (3) introduction of statistical concepts, perhaps akin to those employed in the activated-complex theory of chemical reaction rates. The three approaches are in fact complementary rather than mutually exclusive.

Extensive and invaluable numerical integrations of Type 1 have been performed for triatomic systems.[1–3] They are almost entirely classical mechanical in nature, and serve as exact classical numerical experiments with which more physical approaches of Types 2 and 3 may be compared. In the present paper a theory of Type 3 is formulated for total reaction cross sections. The reactions are quantum or classical and contain three or more atoms. Detailed application to the $H+H_2$ reaction, for example, is made in a subsequent paper.

The present work utilizes the activated-complex concept (this does not imply the existence of any long-lived complex, of course), as well as a quasi-equilibrium postulate for population of the activated complex, and a dynamical postulate: (1) vibrational adiabaticity, where appropriate, and (2) the assumption that only the initial energy of the reaction coordinate (the relative translational motion initially) and of any coupled adiabatic mode can be used to overcome the energy barrier. (The barrier arises from any natural barrier, from the vibrational adiabatic effects, and from any centrifugal contribution.) Thus, the theory has both statistical and dynamical features. They will be discussed in more detail in subsequent publications.

The present study is intended to apply to reactions even when they have steric and activation effects. It differs in that respect from an approach of Light and co-workers described in a recent series of papers.[4] The latter considered cross sections of reactions having centrifugal barriers and discussed the nature of and the energy distribution of the reaction products.

Initially, the theory is presented for simplicity in a form which neglects any diffraction effect along the reaction coordinate near the activated-complex region. In a later section this effect is included. The principal results of the present paper are embodied in Eqs. (10), (15), (25), (28), (30), and (37). Some particular cases of these equations are given in (13), (19), (21), (26), (29), (31), and (38).

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* Supported by a grant from the National Science Foundation at the University of Illinois and by a National Aeronautics and Space Administration Grant NsG-275-62 while the author was a Visiting Professor at the Theoretical Chemistry Institute of the University of Wisconsin.

[1] See, for example, D. L. Bunker and N. C. Blais, J. Chem. Phys. **37**, 2713 (1962); **41**, 2377 (1964), and references cited therein; M. Karplus and L. M. Raff, *ibid.* **41**, 1267 (1964); **44**, 1212 (1966); P. J. Kuntz, E. M. Nemeth, J. C. Polanyi, S. D. Rosner, and C. E. Young, *ibid.* **44**, 1168 (1966). A tetratomic reaction has been treated classically by L. M. Raff, J Chem. Phys. **44**, 1202 (1966). Pioneering computer studies, particularly for collinear collisions, were performed by Wall and his collaborators: F. T. Wall, L. A. Hiller, Jr., and J. Mazur, J. Chem. Phys. **29**, 255 (1958), and subsequent articles. Some quantum-mechanical calculations have been made by E. M. Mortensen and K. S. Pitzer, Chem. Soc. (London) Spec. Publ. **16**, 57 (1962). Recent reviews of experimental results on reactive scattering have been given by D. Herschbach, Advan. Chem. Phys. **10**, 319 (1966), and by E. F. Greene, A. L. Moursund, and J. Ross, *ibid.* **10**, 135 (1966).

[2] M. Karplus, R. N. Porter, and R. D. Sharma, J. Chem. Phys. **43**, 3259 (1965).

[3] For analytic approaches to ion–molecule stripping reactions see A. Henglein, K. Lacmann, and B. Knoll, Chem. Phys. **43**, 1048 (1965). For atom–molecule stripping reactions see R. E. Minturn, S. Datz, and R. L. Becker, *ibid.* **44**, 1149 (1966). Analytic features of these and other reactions are discussed by Herschbach in Ref. 1.

[4] J. C. Light, J. Chem. Phys. **40**, 3221 (1964); P. Pechukas and J. C. Light, *ibid.* **42**, 3281 (1965); J. C. Light and J. Lin, *ibid.* **43**, 3209 (1965); P. Pechukas, J. C. Light, and C. Rankin *ibid.* **44**, 794 (1966). Compare W. B. Maier II, *ibid.* **41**, 2174 (1964), Appendix and references cited therein; C. F. Giese, Advan. Chem. Phys. **10**, 247 (1966), and references cited therein.

In the concluding part of the paper several topics are considered briefly, including reaction probabilities, energy distribution of products, and vibrational nonadiabaticity.

II. TERMINOLOGY

The following terminology is used below for coordinates in the center-of-mass system. Reactants: (a) three translations—one radial and two orbital, (b) adiabatic vibrations or rotations, (c) all others, henceforth called active modes. Activated complex: (a) reaction coordinate q_i, (b) adiabatic vibrations (or rotations) coupled only to q_i throughout the motion, (c) all others, henceforth called active. Adiabatic modes are those which retain their quantum number (or classical action) on formation of activated complex from the reactants. In the $H+H_2$ reaction, for example, the mode which is an H_2 vibration in H_2 and a symmetric stretching in the activated complex H_3 is approximately adiabatic[5,6] at low to moderate relative velocities.

A *locally* adiabatic approximation[6] is used below for all coordinates other than q^r. Adiabaticity *in the large* is assumed only for the adiabatic group of coordinates. The activated complex is defined as that q^r (denoted by q^{r+}) for which $\epsilon_{N^+}(q^r)$, the energy of the rotation–vibration coordinates including potential energy of the q^r motion, has a maximum as a function of q^r. The value at the maximum is denoted by ϵ_{N^+}. This definition of q^{r+} can be shown to reduce to the usual ones in the literature when the particular assumptions appropriate to the latter are introduced.

When the locally separable[6] or locally separable adiabatic approximations[6] are used instead of the locally adiabatic one, the form of the final equations is found to be unaltered. Only the terminology differs.[5,6]

III. NOTATION

q^r	Reaction coordinate
q^{r+}	Value of q^r at the activated complex It may vary with the quantum state N^+
p	Initial momentum of reactants in the center-of-mass system
k	Corresponding wavenumber ($=p/\hbar$)
μ	Reduced mass of the two reactants
E_p	Initial translational energy of reactants in the center-of-mass system ($=p^2/2\mu$)
N	Initial quantum state of pairs of reactants (exclusive of orbital angular momentum l and of its component), N denotes a pair of numbers v, n
v, E_v	Initial quantum state and energy of adiabatic degrees of freedom of pair of reactants, if any
n, E_n	Initial quantum state and energy of active degrees of freedom of pair of reactants
σ_{Np}	Reaction cross section for systems in an initial state N
σ_{vnp}	Reaction cross section for systems in an initial state v, n
Γ	A summation operator involving summation over all geometric and optical isomeric reaction paths from reactants to activated complexes for the given process
V_0	Potential energy of most stable configuration of activated complex minus that for reactants
N^+	Quantum number of activated complex in a given vibration–rotation state N^+
n^+	Quantum number of active modes of the activated complex
ϵ_{N^+}	Minimum energy needed for classical mechanical passage through the coordinate hypersurface, $q^r=q^{r+}$, in state N^+
E_{n^+}	Contribution of active modes to ϵ_{N^+}
ϵ_v^+	Contribution of adiabatic modes and of potential energy of q^r motion to ϵ_{N^+}
$\bar{\epsilon}_v^+$	Average of ϵ_v^+ for the given E
E_v^+	For Cartesian q^r, energy of adiabatic modes in the activated complex ($E_v^+ + V_0 = \epsilon_v^+$ for this Cartesian approximation)
E	Total energy in the center-of-mass system ($=E_v+E_n+E_p=E_{n^+}+\epsilon_{v^+}+$ kinetic energy of q^r motion)
V_c	Centrifugal potential
V_e	$\bar{\epsilon}_v^+ - E_v$
j	Initial rotational angular momentum quantum number. [If the two reactants have individual j's, j_1 and j_2, then j lies in the interval $(\lvert j_1-j_2 \rvert, \cdots, j_1+j_2)$]
$w_{lvnp}{}^J$	Reaction probability of reacting pair with total angular momentum J, initial orbital angular momentum l, and in state specified by v, n, and p
w_{lvnp}	Reaction probability of pair specified by l, v, n, and p
$\omega(E_n)$, $\omega^+(\epsilon_{N^+})$	Number of states n and n^+ per unit energy (i.e., at fixed v) when the energy of the active modes is E_n and when the activated complex is in the state N^+, respectively

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[5] R. A. Marcus, J. Chem. Phys. **45**, 2138 (1966).

[6] R. A. Marcus, J. Chem. Phys. **43**, 1598 (1965).

$\Gamma S(E-E_n)$	$(k^2/\pi)\sigma_{vnp}$ (outside of threshold)
$\Gamma S(E-E_j-E_j^+)$	$(k^2/\pi)\sigma_{vjp}$ (at threshold for an atomic–diatomic molecule reaction)
$Q(s)$	Partition function of active modes of reactant pair when $s=1/kT$, $\sum_n \exp(-sE_n)$
$Q^+(s)$	A "partition function[7]" of an activated complex having a fixed v, $\sum_{n^+} \exp(-s\epsilon_{N^+})$
A, A^+	Constants in classical expressions for $Q(s)$ and $Q^+(s)$, as in Eq. (11)
$A_{\text{rot}}, A_{\text{rot}}^+$	Rotational factors in A and A^+
$N_{\text{vib}}^+(x)$	Number of vibrational states of the active modes of the activated complex when their energy does not exceed x
I, I^+, σ, σ^+	Moments of inertia and symmetry numbers for a diatomic molecule and for a linear activated complex in an atom–diatomic-molecule reaction
κ	Transmission coefficient for the given E and N^+, or given E, v, and n^+

IV. QUASIEQUILIBRIUM EQUATIONS

A quasiequilibrium hypothesis was used elsewhere[8a] to derive (1) for a classical q^r motion:

$$\sum_N (k^2/\pi)\sigma_{Np} = \Gamma \sum_{N^+} 1, \tag{1}$$

where σ_{Np} is the reaction cross section for a pair of reactants which are in an initial vibration–rotation state N and which have an initial relative momentum p. $\sum_N$ and $\sum_{N^+}$ represent sums over all vibration–rotation states of the pair of reactants and of the activated complex, respectively, available to each pair or complex whose total energy is E (e.g., the second sum is over all N^+ for which $\epsilon_{N^+} \leq E$). Γ, a second summation operator, denotes a summation over all optically and geometrically isomeric reaction paths leading to activated complexes for the process.

The adiabatic degrees of freedom (usually vibrational) remain in approximately the same quantum state v during formation of the activated complex. If n denotes the quantum number for the other rotation–vibration degrees of freedom of the reactants and if n^+ denotes that for the other ones of the activated complex, N and N^+ denote the sets (v, n) and (v, n^+), respectively. A sharper form of (1) was then obtained[8b]:

$$\sum_n (k^2/\pi)\sigma_{vnp} = \Gamma \sum_{n^+} 1. \tag{2}$$

$\sum_n$ and $\sum_{n^+}$ represent sums over all active vibration–rotation states of reactant pair and activated complex, respectively, available to each species whose total energy is E and whose adaiabatic modes are in a specified state v.

Quasiequilibrium equations were also given for systems having a given total angular momentum quantum number J and given energy, with (or without) given v.[5] We cite them later as needed. Classical forms of these equations and of (1) and (2) were obtained by converting the multiple sums to multiple integrals over a quantum-number space and then over a classical-action space. A test of (2) has been described elsewhere,[6] utilizing computer results[2] on numerical integration of the equation of motion. Good agreement was found over the range for which data were available.

V. SOME DYNAMICAL AND STATISTICAL CONSIDERATIONS

The contribution of ϵ_v^+ to ϵ_{N^+} may depend on N^+, since q^{r+} may depend on N^+. For a given E, ϵ_v^+ has some suitable average, $\bar{\epsilon}_v^+$, over the states N^+, the nature of which seen from Eq. (10).[8c] The following considerations are introduced here and are discussed in more detail in later papers.

A. Dynamical Condition for Reaction

The adiabatic modes and the q^r motion are strongly coupled, an increase in the energy of the one being compensated by the loss in the other. Their initial energy is E_p+E_v, since at large separation distances the q^r motion is the relative translational motion. At $q^r=q^{r+}$, the energy residing in the adiabatic modes, in the natural barrier, and in the centrifugal barrier is $\bar{\epsilon}_v^+ + V_c$. Consequently, for reaction to occur we assume $E_p+E_v \geq \bar{\epsilon}_v^+ + V_c$, which can be rewritten as

$$E_p \geq V, \tag{3}$$

$$V = V_c + V_e, \tag{4}$$

$$V_e = \bar{\epsilon}_v^+ - E_v. \tag{5}$$

An assumption related to (3) appears in simple collision theory, in that only E_p is assumed to be assumed to be effective in overcoming a barrier.

As discussed at more length in Appendix I, V_c outside of the threshold region is approximately independent of the initial rotational state j, and depends primarily on the initial orbital angular-momentum

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[7] This Q^+ may be regarded only as a "generalized partition function," since q^{r+} may vary with N^+, i.e. since each ϵ_{N^+} may occur at a different value of q^{r+}. It appears in the final expression for the cross section, or for the rate constant, when the q^r motion is treated classically.

[8] (a) Compare Eq. (3) of Ref. 5, plus the supplementary approximation 2 there. (b) Compare Eq. (4) of Ref. 5, plus the supplementary approximation 2 there. (c) For many reactions, as in Sec. VII.A, ϵ_v^+ is essentially independent of N^+; then $\bar{\epsilon}_v^+ = \epsilon_v^+$. For some reactions, as in Sec. VII.C, ϵ_v^+ depends on N^+ because of the dependence of q^{r+} on l and, thereby, of the potential energy term in ϵ_v^+ on l. In Sec. VII.D ϵ_v^+ depends not only on J but also on the "bending mode" quantum number and through it on E.

quantum number l. At threshold, it depends primarily on j and is denoted by E_j^+.

B. Statistical Assumption for Reaction Probability

When the expression for σ_{vnp} in terms of reaction probabilities w_{lvnp}^J [e.g., Eq. (A3) in Appendix II] is introduced into (1) and (2), one sees that a certain sum over reaction probabilities equals a particular sum over quantum states of the activated complex [e.g., Eq. (A6)]. The second sum is a function of E, and we now make the statistical assumption that the contribution of each reaction path (there may be more than one) to a reaction probability w_{lvnp}^J is a function only of the "excess," $E_p-V_e-V_c$, for that $Jlvnp$ and path.

Since $(k^2/\pi)\sigma_{vnp}$ equals a weighted sum over l of w^J's [Eq. (A3)], we obtain at once the following results: Outside of threshold, where V_c depends only on l, the contribution of each path to $(k^2/\pi)\sigma_{vnp}$ becomes a function only of E_p-V_e. At threshold, where V_c was E_j^+, the contribution to $(k^2/\pi)\sigma_{vnp}$ becomes a function only of $E_p-V_e-E_j^+$. An integral equation covering both regions at once is set up (but not solved) in Appendix II. In the body of the present paper we consider separately the regions[9a] away from threshold and at threshold.

In a collision which tends to excite an active mode of the activated complex heavily, there will be less energy in the reaction coordinate available for carrying the system through the activated-complex region, and in some cases the system will not even reach the latter, therefore. The present assumption B takes cognizance of such possibilities in a statistical way.

VI. OUTSIDE OF THE THRESHOLD REGION

According to the preceding argument we may write the contribution of a reaction path to $(k^2/\pi)\sigma_{vnp}$ as a function of $E-E_n$ for a given v, since E_p-V_e equals $E-E_n-\bar{\epsilon}_v^+$. This function, denoted below by $S(E-E_n)$, vanishes when $E-E_n$ becomes less than $\bar{\epsilon}_v^+$. To obtain σ_{vnp} we then sum over all reaction paths. That is,

$$(k^2/\pi)\sigma_{vnp}=\Gamma S(E-E_n). \tag{6}$$

We let $\omega(E_n)$ and $\omega^+(\epsilon_{N^+})$ denote the number of *active modes*' states per unit energy for reactants in state N and for activated complexes in the state N^+, respectively. These ω's refer to fixed v and do not include degeneracy of the adiabatic modes. $\omega^+(\epsilon_{N^+})$ is zero unless ϵ_{N^+} exceeds ϵ_v^+.

Equation (2) now becomes [9b]

$$\int_{E_n=0}^{E} S(E-E_n)\omega(E_n)dE_n$$

$$=\int_{\epsilon_{N^+}=0}^{E}\omega^+(\epsilon_{N^+})d\epsilon_{N^+}\equiv\sum_{n^+}1, \qquad (\epsilon_{N^+}\leq E), \tag{7}$$

where the ϵ_{N^+} integral is performed at fixed v. The ω and ω^+ are sums of δ functions if the active modes are treated quantum mechanically. Otherwise, they are continuous.

Equation (7) is an integral equation for $S(E-E_n)$ and may be solved using Laplace transforms (8):

$$\bar{S}(s)=\int_0^\infty S(x)\exp(-sx)dx, \tag{8a}$$

$$Q(s)=\int_0^\infty \omega(x)\exp(-sx)dx, \tag{8b}$$

$$Q^+(s)=\int_0^\infty \omega^+(\epsilon_{N^+})\exp(-s\epsilon_{N^+})d\epsilon_{N^+}\equiv\sum_{n^+}\exp(-s\epsilon_{N^+}), \tag{8c}$$

where the integration in Q^+ is performed at fixed v and where the summation is over all *quantum states* n^+, the v in N^+ being held fixed.

Multiplication of (7) by $\exp(-sE)$, integration of E from 0 to ∞, use of the convolution theorem of Laplace transforms and of the fact that the transform of the right side of (7) is $Q^+(s)/s$, yields

$$Q(s)\bar{S}(s)=Q^+(s)/s. \tag{9}$$

Inversion yields $S(y)$. One sees from (6) that y is to be set equal to $E-E_n$ to find the contribution of the path to σ_{vnp} for the given v, n, and p. We obtain

$$\sigma_{vnp}=\frac{\pi}{k^2}\frac{\Gamma}{2\pi i}\int_{c-i\infty}^{c+i\infty}\frac{Q^+(s)}{sQ(s)}\exp[s(E-E_n)]ds \tag{10}$$

for $E-E_n\geq\bar{\epsilon}_v^+$; σ_{vnp} is zero otherwise. In (10), c is the usual positive constant, chosen so that the poles of the integrand lie to the left of $s=c$ in the complex plane.

VII. APPLICATIONS OF EQS. (7) AND (10)

Several applications of (7) and (10) are given below. In the first two, q^{r+} is taken to be independent of N^+. (There is frequently a pronounced potential-energy saddle point, which with the aid of a normal mode analysis characterizes a q^{r+} independent of N^+.) The third application is to a well-known situation where only long-range attractive and centrifugal forces occur. Here, q^{r+} depends appreciably on N^+ and the usual

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[9] (a) A system of given j and E is said to be in the threshold region or outside of threshold, roughly speaking, according as J~j or J~l for the weighted average of states contributing to the left-hand sides of Eqs. (1) and (2). (b) Since the integral on the left-hand side of Eq. (7) has some contribution from the threshold region (namely where $E_n=E$) the S function should be replaced by $S(E-E_n-E_j^+)$ for those E_n's, as in Eq. (23) later. However, we ignore the contribution from these E_n's when E is large, i.e., "outside of the threshold region." By solving the integral equation (A2) in Appendix II, this approximation could be eliminated. We plan to explore the solution of (A2).

expression for σ_{vnp} is obtained. In the fourth application an intermediate situation is considered, where there are not only the long-range effects in the third application but also short-range forces and forces restricting the rotational motion of the reactants in the first two.

Previous literature calculations of cross sections with statistical methods have apparently been confined to the third application above and to elementary (hard-sphere) collision theory. [See also Ref. (3).]

A. Active Modes Treated as Classical Harmonic Oscillators

When the active modes (energy E_n, E_{n^+}) are treated classically, when q^{r^+} is independent of N^+, when the vibrations are harmonic, and when rotation–vibration interactions are neglected, the partition functions Q and Q^+ are of the form (11) (since ϵ_v^+ is independent of N^+ in this case, $\bar{\epsilon}_v^+$ becomes ϵ_v^+):

$$Q(s)=A/s^m, \qquad Q^+(s)=(A^+/s^{m+})\exp(-s\epsilon_v^+). \tag{11}$$

Equation (10) then yields

$$\sigma_{vnp}=\frac{\pi}{k^2}\frac{\Gamma A^+}{A}\frac{(E-E_n-\epsilon_v^+)^{m^+-m}}{\Gamma(m^+-m+1)}, \tag{12}$$

where $\Gamma(x)$ is the Γ function of Argument x. A counting of the active modes shows that m^+-m equals 2: In the center-of-mass system the pair of reactants has three translations. The activated complex has one internal translation along the reaction coordinate. Since the pair of reactants and the activated complex have the same number of adiabatic modes, it follows that $m^+-m=2$. Since $E-E_n-\epsilon_v^+$ equals E_p-V_e, we obtain

$$\sigma_{vnp}=(\pi/k^2)(\Gamma A^+/2A)(E_p-V_e)^2. \tag{13}$$

B. Atom Plus Diatomic Molecule (Quantum or Classical Vibrations)[10]

A particularly simple case of (7) or (10) arises when when the reaction involves the formation of a linear activated complex from an atom and a diatomic molecule[10] and when a particular vibration in this collision is adiabatic. The latter vibration would be the one which was originally a vibration in the diatomic molecule and which becomes the symmetric stretching vibration of the linear activated complex. We do not treat the oscillators below as necessarily harmonic or classical.

Equation (15) is first derived from (7). Equation (15) is also appropriate for Case D below, when the reaction treated there is this triatomic one. For this reaction the quantum number n becomes j and its component m_j, and $\omega(E_n)$ becomes A_{rot}, which is $2I/\sigma\hbar^2$ for a diatomic molecule. The quantum number n^+ denotes the totality of rotational and bending vibrational quantum numbers in the activated complex.

A change of variable in (7) from E_j to $x(=E-E_j)$ followed by differentiation of both sides with respect to E leads to

$$S(u)=(\sigma\hbar^2/2I)\omega^+(u) \tag{14}$$

for any u. (To represent S by a smooth function, ω^+ must denote a smoothed function.)

To calculate σ_{vjp}, $S(u)$ is needed at $u=E-E_j$ and (6) is applied. We thus obtain

$$\sigma_{vjp}=(\pi/k^2)(\sigma\hbar^2/2I)\Gamma\omega^+(E-E_j), \tag{15}$$

where $\omega^+(u)$ is the total number of active states n per unit energy when the *total energy* of the activated complex is u.

When rotation–vibration interaction and any dependence of q^{r^+} on N^+ are neglected, $\bar{\epsilon}_v^+$ equals ϵ_v^+ and $\omega^+(u)$ equals the convolution

$$\omega^+(u)=\int_{x=0}^{u-\epsilon_v^+}\omega_{\text{rot}}^+(u-\epsilon_v^+-x)\,\omega_{\text{vib}}^+(x)\,dx, \tag{16}$$

where $\omega_{\text{rot}}^+(y)$ and $\omega_{\text{vib}}^+(x)$ are the numbers of rotational and bending vibrational states per unit energy when the energies of these active modes of the activated complex are y and x, respectively. Since $\omega_{\text{rot}}^+(y)$ equals A_{rot}^+ for all y, i.e., equals $2I^+/\sigma^+\hbar^2$, we then obtain

$$\omega^+(u)=(2I^+/\sigma^+\hbar^2)N_{\text{vib}}^+(u-\epsilon_v^+). \tag{17}$$

$N_{\text{vib}}^+(y)$ is the number of bending vibrational states having an energy less than or equal to y:

$$N_{\text{vib}}^+(y)=\int_0^y\omega_{\text{vib}}^+(x)\,dx. \tag{18}$$

Thus, for these additional assumptions we find

$$\sigma_{vjp}=(\pi/k^2)(\Gamma\sigma I^+/\sigma^+I)N_{\text{vib}}^+(E_p-V_e), \tag{19}$$

where we used the equality, $E-E_n-\epsilon_v^+=E_p-V_e$.

When Case A above is specialized to be this triatomic reaction, and when the vibrations in (19) are classical harmonic oscillators, Eqs. (13) and (19) coincide, as they should.

C. Free Rotation in Activated Complex

When the rotations and vibrations of the reactants are unhindered in passing through an activated-complex configuration, as in some ion–molecule reactions, we may proceed as follows: We may include all vibrations and rotations of the reactants in $Q^+(s)$. $Q^+(s)$ now becomes the product of Q_{int} and Q_l^+, the former being the partition function of the vibration–rotation modes of the reactants and the latter being $\sum_l \exp(-sE_l^+)$,

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[10] These equations also apply to other reactions, $A+BC\rightarrow AB+C$, of the three center type when the internal motions in each center A, B, and C, are neglected. Such an approximation is made in current computer calculations in the literature, for example for the $K+CH_3I$ reaction.[1]

where E_l^+ is the maximum of the function $E_l^+(r)$:

$$E_l^+(r)=(l^2\hbar^2/2\mu r^2)+U(r); \tag{20}$$

$E_l^+(r)$ is the sum of a centrifugal potential and of the potential energy as a function of the separation distance r. Now, q^r is r and q^{r+} is the r which maximizes (20) for the given l. In (20) the difference between l and $l+1$ was neglected. For a barrier such as (20), Γ is typically unity.

In (10) Q is simply Q_{int}, and so cancels the factor Q_{int} in Q^+. Thus, in (10) the internal degrees of freedom of the reactants cancel and we can simply ignore their presence. While (10) can now be solved, it is more convenient to solve (7). With this justified omission of the internal degrees of freedom there are seen to be no contributions to E_n, so that $\omega(E_n)$ equals $\delta(E_n)$ and the left-hand side of (7) becomes $S(E)$. On the right side of (7) only the orbital motion of the activated complex contributes to u, and that side becomes $N_l^+(E_p)$, the number of orbital states for which $E_l^+(r^+)$ does not exceed E_p. If l_m is the maximum value of l for which $E_l^+\leq E_p$, $N_l^+(E_p)$ equals $\int 2ldl$, i.e., l_m^2.

The impact parameter b equals $l\hbar/p$, i.e., l/k. We thus obtain from (7) the well-known result[11] (21), where b_m is the maximum-impact parameter leading to reaction for the given $p(b_m=l_m/k)$.

$$\sigma_{vnp}=\pi b_m^2. \tag{21}$$

D. Restricted Rotation in Activated Complex Having a q^{r+} (N^+)

In this section arguments are sketched which permit one to generalize Cases A and B on one hand, and Case C on the other. We use (7) or (10) as before. In this intermediate case, where the bending vibrations distort Case C and where the dependence of q^{r+} on N^+ distorts Cases A or B, the calculation of

$$\sum_{n^+}\exp(-s\epsilon_{N^+})$$

in (10) becomes more involved. The rigorous procedure, within the framework of the assumptions used to derive (10), is to calculate each $\epsilon_{N^+}(q^{r+})$ by maximizing $\epsilon_{N^+}(q^r)$ with respect to q^r, and then to evaluate (10).

A simpler but less rigorous way to evaluate (10) would be to calculate σ_{vnp} by first evaluating all $\epsilon_{N^+}(q^r)$ at the same q^r and at the given v, then calculating $\sum_{n^+}\exp(-s\epsilon_{N^+})$, and finally finding the q^r which maximizes this sum at the given s. One then calculates σ_{vnp} from (7) or (10).

This second, less rigorous procedure is reminiscent of a method sometime assumed in qualitative discussions in the literature of activated-complex theory: one calculates a free energy of activation, notes that it passes through a maximum as a function of q^r, and defines q^{r+} as the q^r at this maximum. This second procedure is also intimately related to an ingenious one which Bunker[12] has used successfully for unimolecular reactions in obtaining good agreement between computer-calculated rate constants and those obtained from RRKM theory. He defines q^{r+} as that q^r which minimizes the number of quantum states available to the activated complex at the given energy. The detailed relation between these approaches will be discussed elsewhere.

For an atom–diatomic molecule reaction having an adiabatic vibration, Eq. (15) can be used instead of (10), and $\omega^+(E-E_j)$ is evaluated by counting all N^+ (at the fixed v) for which $\epsilon_{N^+}(q^{r+})\leq E-E_j$. Each $\epsilon_{N^+}(q^{r+})$ is computed as in the first paragraph above.

VIII. APPROXIMATE THRESHOLD BEHAVIOR

In Appendix III an integral equation is set up for the general reaction at threshold, but in this section is considered the atom–diatomic-molecule reaction[10] described earlier in Case B.

As noted earlier, the contributions of any reaction to $(k^2/\pi)\sigma_{vnp}$ is taken to be a function of $E_p-V_e-E_j^+$ and so of $E-E_n-E_j^+$ at the given v. This function is denoted by $S(E-E_n-E_j^+)$, and we have

$$(k^2/\pi)\sigma_{vjp}=\Gamma S(E-E_n-E_j^+). \tag{22}$$

Equation (2) leads again to (7), but now with $S(E-E_n)$ replaced by $S(E-E_n-E_j^+)$. Since $\omega(E_n)$ equaled A_{rot} for this reaction and n denoted (j, m_j), we find

$$A_{\text{rot}}\int_{E_j=0}^{E}S(E-E_j-E_j^+)dE_j=\int_{\epsilon_{N^+}=0}^{E}\omega^+(\epsilon_{N^+})d\epsilon_{N^+}, \tag{23}$$

where the integration on the right is at constant v. (Since S vanishes when $E_j>E-\bar{\epsilon}_v^+-E_j^+$, there was no error in writing the upper limit of E_j as E.)

Introduction of a change of variable from E_j to $x(=E-E_j-E_j^+)$, so that $dx=-dE_j(I^++I)/I^+$, leads to (24), where it was valid to replace the lower limit of $x=-IE/I^+$ by $x=0$ since S is zero in the interval $(-IE/I^+,0)$:

$$\frac{A_{\text{rot}}I^+}{I^++I}\int_{x=0}^{E}S(x)dx=\int_{\epsilon_{N^+}=0}^{E}\omega^+(\epsilon_{N^+})d\epsilon_{N^+}. \tag{24}$$

Differentiation of both sides with respect to E yields an expression for $S(u)$ for any u. Upon evaluating it at $u=E-E_j-E_j^+$ and using (22) we obtain (25) as the threshold counterpart of (15):

$$\sigma_{vjp}=(\pi/k^2)[\Gamma\sigma\hbar^2(I^++I)/2II^+]\omega^+(E-E_j-E_j^+). \tag{25}$$

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[11] For example, for ion–molecule reactions see G. Gioumousis and D. P. Stevenson, J. Chem. Phys. **31**, 1338 (1959), who use an $1/r^4$ long-range attractive potential. D. A. Kubose and W. H. Hamill, J. Am. Chem. Soc. **85**, 195 (1963) added a short-range repulsive potential to $U(r)$, and T. F. Moran and W. H. Hamill, J. Chem. Phys. **39**, 1413 (1963) added an oriented dipole term. The possible influence of restricted rotation at short distances apparently has not been treated until Application D below.

[12] D. L. Bunker (private communication).

Upon neglect of rotation–vibration interaction and dependence of q^{r^+} on N^+, (17) may be introduced into (25), yielding

$$\sigma_{vjp}=(\pi/k^2)[\Gamma\sigma(I^+ + I)/\sigma^+ I]N_{\mathrm{vib}}{}^+(E_p - V_c - E_j{}^+). \tag{26}$$

Because of the condition mentioned earlier,[9a] Eq. (22) and, hence, (25) and (26) are appropriate only when both E and E_j are small.

Equation (26) may be compared with (19). Their difference outside of the threshold region ($E_p - V_c \gg E_j{}^+$) is slight when $I^+ \gg I$. A formula encompassing (25) and (15) could be obtained by solving an integral equation based on a stronger form of the quasiequilibrium hypothesis,[5] one for systems with a given total angular momentum, given in Appendix II. Tabulations of the computer-calculated reaction probabilities w^J defined there would be useful in analyzing relevant dynamical postulates.

IX. QUANTUM-MECHANICAL q^r MOTION

Treatment of the motion along q^r in a quantum-mechanical and curvilinear manner led to Eqs. (1) and (2), but with the $\sum 1$'s replaced by $\sum \kappa$'s.[5] In Eq. (1) this κ is the transmission coefficient for the given E and N^+; in Eq. (2) it is that for the given E, v, and n^+.

Because of quantum-mechanical tunneling the condition $E_p \geq V$, can no longer be imposed. However, we may still regard the contribution of each path to $(k^2/\pi)\sigma_{vnp}$ as a function of $E-E_n$, but now we must permit the occurrence of negative values of $E-E_n-\bar{\epsilon}_v{}^+$.

When the q^r motion is treated as Cartesian,[13] the transmission coefficient κ can be written as a function of the energy of the q^r motion ($E-E_{n^+}-E_{v^+}$) minus the potential-energy maximum V_0. That is, κ can be written as a function of $E-E_{n^+}-\epsilon_v{}^+$, i.e., of $E-\epsilon_{N^+}$. When the curvilinear nature of q^r is not neglected, but when only the coupling of the adiabatic coordinates to q^r is considered, κ depends on $E-\epsilon_{N^+}$ and v, i.e., we may write $\kappa(E-\epsilon_{N^+}, v)$.[14] The dependence on v is weak.

There is an upper limit to ϵ_{N^+}, the exact value of which is determined (in a locally adiabatic approximation) by the value which makes the kinetic energy of the q^r motion negative even outside the barrier region. For practical purposes, however, since κ decreases rapidly with decreasing energy of q^r motion, this upper limit for ϵ_{N^+} can normally be taken as ∞. When a more precise limit is needed it can be calculated in this locally adiabatic approximation.

We thus obtain (27) instead of (7), for a Cartesian q^r, while for curvilinear q^r $\kappa(E-\epsilon_{N^\cdot})$ would be written as $\kappa(E-\epsilon_{N^+}, v)$:

$$\int_0^E S(E-E_n)\omega(E_n)dE_n=\int_0^\infty \omega^+(\epsilon_{N^+})\kappa(E-\epsilon_{N^+})d\epsilon_{N^+}. \tag{27}$$

[The classical result (7) follows from (27) when one sets $\kappa(x)=1$ for $x\leq 0$ and $\kappa(x)=0$ for $x>0$.]

Equation (27) can be inverted, but the results become complex, and we shall limit the following remarks to the atom–diatomic-molecule reaction[10] considered earlier. Since now $\omega(E_n)$ equals $2I/\sigma\hbar^2$, a change of variable from E_n to $x=E-E_n$ and differentiation with respect to E leads to an expression for $S(u)$ for any u. From (6) one then obtains

$$\sigma_{vjp}=\frac{\pi}{k^2}\frac{\sigma\hbar^2}{2I}\Gamma\left[\frac{d}{dy}\int_0^\infty \omega^+(\epsilon_{N^+})\kappa(y-\epsilon_{N^+})d\epsilon_{N^+}\right], \tag{28}$$

where y is $E-E_j$. When rotation–vibration interaction and the dependence of q^{r^+} on N^+ are neglected (17) may be used and (28) becomes

$$\sigma_{vjp}=\frac{\pi\Gamma}{k^2}\frac{\sigma I^+}{\sigma^+ I}\left[\frac{d}{dy}\int_0^\infty N_{\mathrm{vib}}{}^+(\epsilon_{N^+}-\epsilon_v{}^+)\kappa(y-\epsilon_{N^+})d\epsilon_{N^+}\right], \tag{29}$$

where y is $E-E_j$.

In the threshold region Eq. (27) applies, but with $S(E-E_n)$ replaced by $S(E-E_n-E_j{}^+)$. On utilizing some remarks which led from (23) to (24), we obtain (30) for the atom–diatomic-molecule reaction considered previously:

$$\sigma_{vjp}=\frac{\pi\Gamma}{k^2}\frac{\sigma\hbar^2(I^+ + I)}{2II^+}\left[\frac{d}{dy}\int_0^\infty \omega^+(\epsilon_{N^+})\kappa(y-\epsilon_{N^+})d\epsilon_{N^+}\right], \tag{30}$$

where y is $E-E_j-E_j{}^+$. When the rotation–vibration interaction and the dependence of q^{r^+} on N^+ are neglected (30) yields

$$\sigma_{vjp}=\frac{\pi}{k^2}\frac{\Gamma\sigma(I^+ + I)}{\sigma^+ I}\times\left[\frac{d}{dy}\int_0^\infty N_{\mathrm{vib}}{}^+(\epsilon_{N^+}-\epsilon_v{}^+)\kappa(y-\epsilon_{N^+})d\epsilon_{N^+}\right], \tag{31}$$

where y is $E-E_j-E_j{}^+$.

X. REACTION PROBABILITIES

Reaction probabilities w_{lvnp} for a given orbital angular momentum l can be estimated as follows: Outside of the threshold region Eq. (32)[15] is to be solved using the previously derived expressions for σ_{vnp} and an

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[13] Compare Ref. 5, Supplementary Approximation 1.

[14] Compare Ref. 5, Supplementary Approximation 5, and Ref. 6 for some discussion of the determination of z.

[15] The standard equation (32) is given, for example, in L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Addison-Wesley Publ. Co., Inc., Reading, Mass., 1958), p. 437. Compare Appendix I of Ref. 5.

assumption about w_{lvnp}:

$$\sigma_{vnp}=\frac{\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)w_{lvnp}. \tag{32}$$

The centrifugal potential V_c in the activated-complex region at energies outside of the threshold region is denoted below by E_l^+, which equals $l(l+1)\hbar^2/2I^+$, since $J\cong l$ here. As discussed earlier, for a given v, the contribution of any path to $(k^2/\pi)\sigma_{vnp}$ is taken to be a function of $E-E_n$, vanishing when $E-E_n\leq\epsilon_v^+$, and the contribution to w_{lvnp} is taken to be a function of $E-E_n-E_l^+$, vanishing when $E-E_n-E_l^+\leq\epsilon_v^+$. This contribution is written as $w(E-E_n-E_l^+)$. We have

$$w_{lvnp}=\Gamma w(E-E_n-E_l^+). \tag{33}$$

Equation (10), or a particular case of it, such as Eq. (13), can be introduced into (32) for σ_{vnp}, the former leading to a complex expression. In the case of an atom–diatomic-molecule reaction[10] (15) can be introduced into (32), yielding

$$\frac{\sigma\hbar^2}{2I}\omega^+(E-E_n)=\int_{l=0}^{l_{\max}}w(E-E_n-E_l^+)2l\,dl, \tag{34}$$

where $l_{\max}$ is the l for which $E-E_n-E_l^+=\epsilon_v^+$. On making a change of variable from l to $x=E-E_n-E_l^+$ neglecting rotation–vibration interaction and differentiating (34) with respect to E one obtains

$$w(u-\epsilon_v^+)=(\hbar^2/2I^+)(\sigma\hbar^2/2I)d\omega^+(u)/du \tag{35}$$

for any u. From (33) we then obtain

$$w_{lvjp}=(\Gamma\hbar^2/2I^+)(\sigma\hbar^2/2I)d\omega^+(y)/dy, \tag{36}$$

where $y=E-E_j-E_l^+-\epsilon_v^+$. With rotation–vibration interaction and dependence of q^{r+} on N^+ neglected, use of (17) yields

$$w_{lvjp}=(\Gamma\sigma\hbar^2/2I\sigma^+)[dN_{\mathrm{vib}}^+(E-E_j-E_l^+-\epsilon_v^+)/dE]. \tag{37}$$

It should be emphasized that Eq. (36) implies (15) but not conversely: The starting point of (15) could be a postulate that $(k^2/\pi)\sigma_{vnp}$ is a function of $E-E_n$, without motivating this postulate (as we did earlier) by postulating that w_{lvnp} is a function of $E-E_n-E_l^+$. Because w_{lvnp} represents a finer-grained description than σ_{vnp}, Eq. (36) may be less accurate than (15).

XI. ENERGY DISTRIBUTION OF PRODUCTS

The energy distribution of reaction products has been subjected to extensive investigation, both in experiments and in computer studies.[1–4] The results are of particular interest in strongly exothermic reactions, because of the large amounts of energy available for distribution.

For such exothermic reactions with little activation energy the activated complex normally occurs long before the system reaches the strongly curved part of the reaction path in a space of mass-weighted coordinates. In a statistical-dynamical treatment, the calculation of energy distribution of reaction products can then be decomposed in two parts: (1) calculation of the reaction probabilities $w_{lvnp}{}^J$ or w_{lvnp}, as in the preceding section, and (2) calculation of the subsequent energy redistribution for each initial *Jlvnp* or *lvnp* state. This second step involves additional statistical or dynamical postulates. They are explored in a subsequent paper.

XII. VIBRATIONAL NONADIABATICITY

When the q^r motion is sufficiently slow in a dynamically critical region, the vibration discussed earlier in the A+BC reaction is expected to be adiabatic. A dynamically critical region is one where either the frequency of this vibration is changing appreciably or where the q^r coordinate curve becomes significantly curved, so that coupling of the q^r motion with the vibration may become appreciable in either case. This curvilinear effect is probably a principal source of nonadiabaticity for this particular vibration.

At very high q^r velocities this vibration will no longer remain in the same state: the collision dynamics at a curved part of the reaction path show that q^r kinetic energy will usually be converted into vibrational. The preceding formulas might still be used as a first approximation, perhaps, provided ϵ_{N^+} now denotes the fixed energy (adiabatic or otherwise), i.e., the energy not available for distribution among other modes. A calculation of this quantity and of the velocities for which such nonadiabatic effects become important will be described in a later paper.

ACKNOWLEDGMENTS

A portion of the present work was done while the author was a Visiting Professor at the Theoretical Chemistry Institute of the University of Wisconsin during the summer of 1965. The author especially enjoyed the hospitality of Professor Hirschfelder, Professor Bernstein, and their colleagues during that stimulating visit.

APPENDIX I: THE CENTRIFUGAL POTENTIAL, V_c

Bimolecular gas-phase reactions of particular interest in applications of activated-complex theory have usually been of the three center type, A+BC→AB+C, where A is H, CH_3, Cl, etc., B is an H, a halide, etc., and R is any of these.

Often, two moments of inertia of the activated complex are much larger than the third and are approximately equal. (Linear activated complexes are automatically included, thereby.) The two rotations involving these two moments of inertia (I^+) arise partly from the relative orbital motion of the two reactants.

At large distances, the centrifugal barrier is

$$l(l+1)\hbar^2/2\mu r^2,$$

where r is the distance of separation. At smaller distances it goes over into $(P_1^{+2}+P_2^{+2})/2I^+$, where P_1^+ and P_2^+ are angular-momentum components about the two axes mentioned above for the activated complex. Since $(P_1^{+2}+P_2^{+2})$ equals the square of the angular momentum, $J(J+1)\hbar^2$, minus the square of its third component along the figure axis of the "symmetric top" $K^2\hbar^2$, the centrifugal barrier V_c is

$$[J(J+1)-K^2]\hbar^2/2I^+$$

and denoted by V_c^J. When the vibrational angular momentum is neglected in the case of a linear activated complex, this V_c^J becomes $J(J+1)\hbar^2/2I^+$.

When the barrier is only centrifugal, the activated complex normally occurs at large r. (Otherwise, other forces enter at small r, and the barrier would not be entirely centrifugal.) In this case the activated complex is the hypersurface $r=r_0$, a constant, where r_0 depends on p. The value of I^+ is μr_0^2, and that of V_c is $l(l+1)\hbar^2/2I^+$, which we designate as V_c^l.

Thus, V_c for the activated complex is V_c^l if the complex occurs at large r and V_c^J if it occurs at small r. In between, it has intermediate values, less well defined perhaps, which depend on extent of rotation-orbital coupling at those r's.

Outside of the threshold region l is typically much greater than j, the rotational quantum number of the reactants. j will add to or substract from l so that, on the average $J\cong l$. In the threshold region the system just has barely enough energy to react, so that states for which V_c is small will be favored. These states are those with $l\cong 0$, and in this case J no longer averages about l but rather, at threshold, is expected to approximate j.

Even for reactions which have only a centrifugal barrier at typical p's, the decrease of p shifts the position of the activated complex to lower r's, and eventually to r's so small that torques and coupling with rotations occur and, ultimately, therefore, the centrifugal part of the barrier becomes V_c^J with $l\cong 0$ and $J\cong j$.

APPENDIX II: AN INTEGRAL EQUATION FOR ENTIRE RANGE

For reacting pairs having a given energy and a given total angular-momentum quantum number

$$J(J=|j-l|\text{ to }j+l)$$

the quasiequilibrium hypothesis yielded (A1).[5] Equation (A1) is a stronger form of this hypothesis than (2) and includes it:

$$\sum_{n^*}\sum_{j}\sum_{l=|J-j|}^{J+j} w_{lvn^*jp}{}^J=\Gamma\sum_{n^{*+}}1, \tag{A1}$$

where n^* denotes the quantum numbers in n, exclusive of j and m_j, and where n^{*+} denotes those in n^+, exclusive of J and its component M. $w_{lvn^*jp}{}^J$ is the probability of a reaction of a system having a given lvn^*jp and, by suitable combination of m_j's, m_l's and Clebsch–Gordan coefficients, is prepared in a state of given J and M. w^J is independent of M. In (A1) j lies in $|j_1-j_2|$ to (j_1+j_2).

If it is assumed that the contribution of a path to w^J is a function of the "energy excess" $E_p-V_e-V_c$, where V_c is given in Appendix I, and call it $w(E-E_{n^*}-V_c)$ for the given v, we have w^J equal to $\Gamma w(E-E_{n^*}-V_c)$ and obtain (A2) from (A1):

$$\sum_{n^*}\sum_{j}\sum_{l=|J-j|}^{J+j} w_{lvn^*jp}{}^J(E-E_{n^*}-V_c)=\sum_{n^{*+}}1. \tag{A2}$$

This integral equation is to be solved for the w^J's. The cross section σ_{vnp}, averaged over all m_j for this j_1, j_2, and j, is then obtained from (A3)[16] (m_j is the component of j along some axis):

$$\sigma_{vnp}=\frac{\pi}{k^2}\Gamma\sum_{J=0}^{\infty}(2J+1)\sum_{l=|J-j|}^{J+j} w_{lvn^*jp}{}^J. \tag{A3}$$

Presentation of the computer data in the form of w^J's would provide information on the assumption that they depend primarily on $E_p-V_e-V_c$. We do not attempt to solve (A2) here, but numerical solutions would be of interest for comparison with computer data on w^J's.

APPENDIX III: AN INTEGRAL EQUATION AT THRESHOLD

Equation (23) is a particular case of Eq. (A6) below.

When the two reactants have rotational angular-momentum quantum numbers j_1 and j_2, j lies in the range $|j_1-j_2|,\cdots,j_1+j_2$, and has an *a priori* probability of occurrence of $(2j+1)/(2j_1+1)(2j_2+1)$. For a given n, and thereby for a given j_1 and j_2, the number j cannot exceed j_1+j_2. Nor can it exceed j^*, the highest value of j satisfying (A4):

$$E_j^+\leq E-E_n-\epsilon_v^+. \tag{A4}$$

Thus, if $j_{\min}$ denotes the lesser of these two quantities,

$$j_{\min}=\text{minimum of }(j_1+j_2,j^*), \tag{A5}$$

the above arguments now lead from (2) to (A6), where the last integral is at fixed v.

$$\int_{E_n=0}^{E}\left[\frac{\omega(E_n)}{(2j_1+1)(2j_2+1)}\times\sum_{j=|j_1-j_2|}^{j_{\min}}(2j+1)S(E-E_n-E_j^+)\right]dE_n=\int_{u=0}^{E}\omega^+(u)\,du, \tag{A6}$$

where u is ϵ_{N^+} and where $S(E-E_n-E_j^+)$ is the contribution of the path to $(k^2/\pi)\sigma_{vnp}$.

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[16] This equation follows from Eq. (4.12) of J. M. Blatt and L. C. Biedenharn [Rev. Mod. Phys. 24, 258 (1952)], when appropriate identification of the symbols is made.