

Analytical Mechanics of Chemical Reactions. IV. Classical Mechanics of Reactions in Two Dimensions*

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The natural collision coordinates of Part III are used to treat the analytical mechanics of chemical reactions, $AB+C \rightarrow A+BC$. Other than in Part II, the classical analytical mechanics of chemical reactions on a smooth potential surface have not been explored previously in the literature. A Hamilton-Jacobi formalism is used, apparently for the first time in calculating a reaction rate. The "vibrationally adiabatic" reaction serves as the zeroth-order approximation and nonadiabatic corrections are obtained. Theoretical expressions yield the rotational and vibrational energy distribution of reaction products, angular distribution, and reaction probability, as a function of impact parameter, initial translational velocity of relative motion, and initial rotational-vibrational state of reactants. The results are not intended to apply to reactions which show very large excursions from vibrational adiabaticity. In the zeroth approximation (vibrational adiabaticity), an adiabatic separation of variables is achieved. Here, the vibrational action is constant; however, the rotational-orbital action changes by a known increment from one constant value to another, on transition of that motion into a bending vibration. The resulting "adiabatic" correlation shows several interesting features. For reactions in which there are no large mass ratios, the state of vibration of AB, of rotation of AB, and of orbital motion of AB+C correlate with the state of vibration of BC, of rotation of BC, and of orbital motion of A+BC, respectively. For reactions with unusual mass ratios, such as $H+Cl_2 \rightarrow HCl+Cl$, the correlation equations show instead the "adiabatic" transformation of Cl_2 rotation into $HCl+Cl$ orbital motion, thereby reflecting the expected result of angular momentum conservation. Had the rotational-orbital cross term in the kinetic energy been neglected, an incorrect correlation would have resulted in the latter case. Extension of the present work to three dimensions involves an added approximation, to be given in a subsequent paper. The expressions and method also permit comparison of one- and two-dimensional computer results on a more similar basis and, because of certain similarities in computer results for energy distributions in two and three dimensions, perhaps comparison with experimental results on energy distributions. In conjunction with the computer results information can be obtained on various approximations, such as near adiabaticity. The present theory can also be used to analyze and perhaps extend various statistical-type theories in the literature.

Numerical integrations of the classical mechanical equations of motion of atoms in a chemically reactive collision have been performed with electronic computers for a variety of dimensions: collisions on a line, in a plane, and in three dimensions.¹⁻⁴ The internal energy distribution of reaction products showed some similarity in each case.⁵

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¹ F. T. Wall, L. A. Hiller, Jr., and J. Mazur, *J. Chem. Phys.* **29**, 255 (1958); **35**, 1284 (1961); F. T. Wall and R. N. Porter, *ibid.* **39**, 3112 (1963).

² (a) N. C. Blais and D. L. Bunker, *J. Chem. Phys.* **37**, 2713 (1962); **39**, 315 (1963). (b) D. L. Bunker and N. C. Blais, *ibid.* **2377** (1964).

³ (a) M. Karplus and L. M. Raff, *J. Chem. Phys.* **41**, 1267 (1964); (b) L. M. Raff and M. Karplus, *ibid.* **44**, 1212 (1966); (c) M. Karplus, R. N. Porter, and R. D. Sharma, *ibid.* **43**, 3259 (1965); (d) L. M. Raff, *ibid.* **44**, 1202 (1966).

⁴ (a) P. J. Kuntz, E. M. Nemeth, J. C. Polanyi, S. D. Rosner, and C. E. Young, *J. Chem. Phys.* **44**, 1168 (1966); (b) J. C. Polanyi and S. D. Rosner, *ibid.* **38**, 1028 (1963); (c) K. G. Anlauf, P. J. Kuntz, D. H. Maylotte, P. D. Pacey, and J. C. Polanyi, *Discussions Faraday Soc.* **44**, 183 (1967).

⁵ A similarity in vibrational and rotational energy distributions of products in two and three dimensions was noted in Refs. 2b and 3a. In Ref. 2b (Fig. 9) a difference occurred in the rotational distribution for 2D and 3D systems in the region of small final j , perhaps reflecting a phase space volume element effect which makes small final j 's less important in the 3D case. This difference did not appear in Ref. 3a (compare Figs. 2 and 7), perhaps because of the different way of plotting the results, one which tends to cancel this possible effect. In both cases, significant out-of-plane scattering caused differences in angular distribution in 2D and 3D. An indirect comparison of 1D with 2D cases in Ref. 4a indicated a similarity in vibrational energy distribution of reaction product here also.

In the present paper the analytical classical mechanics are treated for reactions in a plane. The corresponding quantum-mechanical treatment is given later. Use is made of a novel coordinate system (natural collision coordinates) introduced in Part I for reactions on a line and later extended in Part III to reactions in two or three dimensions.⁶

Other than in Part II, the classical analytical mechanics of chemical reactions on a smooth potential surface have not been explored previously in the literature. The Hamilton-Jacobi equation is utilized in the present paper, apparently for the first time in reaction dynamics, with "vibrational adiabaticity" as the zeroth-order approximation for all quasiperiodic motions; nonadiabatic corrections are also calculated. Extension to three dimensions involves an added approximation and is considered in a later paper.

Because of the similarity noted⁵ in the numerical computations of vibrational-rotational energy distributions of reaction products in two and three dimensions, the results for these particular properties obtained in the present paper may already be compared with experimental results, except perhaps at low j . Such a comparison would be most useful, however, after extensive comparison of numerical 2D and 3D computer results has been made. It should be emphasized that the present theory is designed for reactions

⁶ (a) R. A. Marcus, *J. Chem. Phys.* **45**, 4493 (1966) (Part I); (b) **45**, 4500 (1966) (Part II); (c) **48**, 2610 (1968) (Part III), preceding article.

which do not show large excursions from "vibrational adiabaticity."

A second type of application of the present dynamical results is to statistical-type theories, in particular to obtain insight into their validity and to extend them. Some discussion is given in one of the concluding sections; a more detailed analysis will be given separately.

The present paper is divided into several parts. The first, containing Eqs. (1)–(21), describes an adiabatic separation of variables. The next, containing Eqs. (22)–(100), describes action-angle formalism for the various degrees of freedom, both for the adiabatic approximation and for nonadiabatic corrections thereto. The remaining part of the paper outlines briefly applications to several topics.

GLOSSARY OF SYMBOLS

(Defined in Approximate Order of Appearance)

T_0, T_1	Leading and correction term in kinetic energy
μ	An effective mass, $[m_A m_B m_C / (m_A + m_B + m_C)]^{1/2}$
z, Z, Z_p	Mass-scaled coordinate axes in Fig. 1. $z = (z_B - z_A)/c$; $Z = (z_C - z_{AB})/c$; $Z_p = (z_{BC} - z_A)/c_p$, where z_a = body-fixed z coordinate of atom a ; z_{AB} refers to center of mass of AB; $c = \left[\frac{m_A m_B (m_A + m_B + m_C)}{m_C (m_A + m_B)^2} \right]^{1/4}$
	c_p is c with A and C interchanged
$\kappa(s)$	Instantaneous curvature of Curve C in Fig. 1
n, m	Coordinates, defined in terms of Curve C in the internal coordinate subspace given by Fig. 1 (n is the x in Part I).
s	Reaction coordinate, defined as the arc length along Curve C
r, γ	Coordinates related to m, n . $n = r_0 - r \cos \gamma$, $m = r \sin \gamma$. On Curve C $r = r_0$ and $\gamma = 0$. [Compare (10) in III]
ρ	Vibrational coordinate, $r_0 - r$
ρ_0	Defined in (79)
F	Defined in Ref. 8 and in remark preceding Eq. (9). $F = \mp 1$ at $s = \mp \infty$
$R(s)$	$= (I_{zz}/\mu)^{1/2}$, where I_{zz} is one of the two larger moments of inertia of the system, as in Eq. (22) of III. (R is the distance from 0 in Fig. 1 to any point in the space.)
$R_0(s)$	Value of R at $\rho = \gamma = 0$, i.e., on Curve C
ϕ	Coordinate defining orientation of the system

η	After Eq. (9), η is $1 + \kappa\rho$. Before (9) it is as defined in (20) of Part III
p_i	Momentum conjugate to coordinate q^i
E, H	Total energy, Hamiltonian, respectively
W	Hamilton's characteristic function in (4) or that in (31)
W', W_k	Various contributions to W [Eqs. (6), (8), (12)]
V	Potential energy
$V_1(s)$	Value of V on Curve C, as a function of s
$V_2(\rho, \gamma, s)$	Increment in V on going from curve C (for which $\gamma = \rho = 0$) to any other point $V_2(0, \gamma, s)$
V_2^0	
$\alpha_K(s)$	Quasiconstant of separation in Eqs. (11) and (14)
$\epsilon_\gamma(s)$	Rotational-orbital energy
$\epsilon_\rho(s)$	A quasiconstant of separation in (14)
$\lambda(s)$	$1 - (Fr_0/R_0)^2$
$b(s)$	Fr_0^2/R_0^2
E_γ	Defined by (19)
I	$\mu r_0^2 \lambda$
$\oint p_i dq^i = J_i$	Action variable for i th coordinate at any s , i.e., the phase integral or integral over a period of the q^i motion, at any s
J_γ, J_γ^i	J_γ at rotational and librational side of a rotational-librational boundary, respectively
$\mathcal{H}$	Hamiltonian describing adiabatic motion at any s , defined by (30)
$\tilde{\mathcal{H}}$	Hamiltonian containing adiabatic $s(t)$ and related to $\mathcal{H}$ by (36)
w_i	Angle variable for the q^i motion
$\nu_i(s)$	Frequency of the q^i motion, $\partial \mathcal{H} / \partial J_i$, at any s
W^*	A generating function defined by (37)
δ_i	Phase, e.g., in (34) or (42)
$A(s)$	Potential-energy barrier for the γ motion at any s
k^2	Reduced γ barrier defined in (46)
$F(\frac{1}{2}\gamma, k)$, $E(\frac{1}{2}\gamma, k)$	Normal elliptic integrals of first and second kind
$K(k), E(k)$	Corresponding complete elliptic integrals
$\gamma_0(s)$	Librational limit of γ , defined by (55)
k_1	$1/k$
K_1, D_1	$K(k_1), D(k_1); D_1 = (K_1 - E_1)/k_1^2$
β	$\sin^{-1}(k_1^{-1} \sin \frac{1}{2}\gamma_0)$
u	$2w_\gamma K(k)$ in (68)
u_0, u_1	$4w_\gamma F(\frac{1}{2}\gamma_0, k)$ in (74) and $4w_\gamma K(k_1)$ in (75)
$Z(u)$	Jacobian zeta function
B	IA
$U(\rho, s)$	Eq. (78)
ω^2	Eq. (80)
ϵ	ρ vibrational energy [Eq. (81)]
a	Eq. (90)
g	Integrand in (97)

¹⁰ H. C. Corben and P. Stehle, *Classical Mechanics* (John Wiley & Sons, Inc., New York, 1960), 2nd ed., Chap. 11.

ADIABATIC APPROXIMATION

An adiabatic approximation for the ρ and γ motions is introduced by setting

$$W'(\rho, \gamma, s) = W_1(s) + W_2(\rho, \gamma; s) \quad (8)$$

and neglecting the derivatives of W_2 with respect to s ; W_2 depends on ρ and γ but only weakly on s in an adiabatic approximation.

As in the usual treatment of molecular structure problems vibration-rotation interactions (ρ , ϕ and ρ , γ) are neglected initially. They can be included later by a perturbation method if desired. To this end the r , R , and F in the coefficients in T_0 are replaced by their values at $\gamma = \rho = 0$, i.e., by functions of s alone, $r_0(s)$, $R_0(s)$, and $F(s)$, respectively; $V_2(\rho, \gamma, s)$ is approximated by (10), a step which neglects the (ρ, γ) interaction potential energy, and η is replaced by its value at $\gamma = 0$, denoted below by η :

$$\eta = 1 + \kappa\rho. \quad (9)$$

Here, $\kappa(s)$ is the instantaneous curvature of Curve C in Fig. 1, at any s . That is, for notational simplicity we continue to use the symbols F and η , but with the restricted definitions just cited. This η has the same meaning as in Parts I and II,

$$V_2(\rho, \gamma, s) \cong V_2(0, \gamma, s) + V_2(\rho, 0, s). \quad (10)$$

(Alternative to the above zeroth-order approximations would be one where the ρ motion is adiabatic with respect to both the γ and s motions.)

After introduction of (8)–(10) into (7) the dW_1/ds term is placed on the right side of the equation, all other terms are placed on the other side, and both sides multiplied by η^2 . The right side is now independent of γ and ρ , and so both sides are set equal to an s -dependent parameter, $\alpha_K(s)$, for an adiabatic separation of variables.¹¹ The s equation is then

$$(2\mu)^{-1}(dW_1/ds)^2 = \alpha_K(s). \quad (11)$$

In the new ρ, γ equation one may now set

$$W_2(\rho, \gamma; s) = W_3(\rho; s) + W_4(\gamma; s), \quad (12)$$

where W_3 and W_4 depend on ρ and γ , respectively, and more weakly on s . In this new ρ, γ equation all terms dependent on γ (and on s) are then placed on one side of the equation and all terms dependent on ρ (and s) on the other. Both sides may then be set equal to an s -dependent parameter, $\epsilon_\gamma(s)$, yielding

$$(2\mu r_0^2)^{-1} \left(\frac{dW_4}{d\gamma} \right)^2 + (2\mu R_0^2 \lambda)^{-1} \left(p_\phi - F \frac{dW_4}{d\gamma} \right)^2 + V_2(0, \gamma, s) = \epsilon_\gamma(s), \quad (13)$$

¹¹ This α_K is the same as the $\alpha_2 - V_1$ in Part II. The α_1 in Eq. (10) there corresponds to the present $E - \epsilon_\gamma$.

and

$$(2\mu)^{-1}(dW_3/d\rho)^2 + V_2(\rho, 0, s) + [\alpha_K(s)/\eta^2] = \epsilon_\rho(s), \quad (14)$$

where λ and ϵ_ρ are defined by

$$\lambda = 1 - (Fr_0/R_0)^2 \quad (15)$$

and

$$E = V_1(s) + \epsilon_\gamma(s) + \epsilon_\rho(s). \quad (16)$$

The adiabatically separated equations are Eqs. (11), (13), and (14).

When Eq. (13) is rewritten as

$$(2I)^{-1}[(dW_4/d\gamma) - b p_\phi]^2 + V_2(0, \gamma, s) = E_\gamma, \quad (17)$$

where

$$I = \mu r_0^2 \lambda, \quad (18)$$

$$E_\gamma = \epsilon_\gamma - p_\phi^2/2\mu R_0^2, \quad (19)$$

$$b = Fr_0^2/R_0^2, \quad (20)$$

the quadratic equation (17) is immediately solved for $dW_4/d\gamma$,¹²

$$p_\gamma = dW_4/d\gamma = b p_\phi + \{2I[E_\gamma - V_2(0, \gamma, s)]\}^{1/2}. \quad (21)$$

Integration of the second equality yields W_4 . Since ϕ is absent in the Hamiltonian, p_ϕ is a constant.

We note that $\epsilon_\gamma(s)$ is the energy of the γ, ϕ motion [Eq. (13)], and $\epsilon_\rho(s) + V_1(s)$ is the energy of the ρ, s motion [cf. Eq. (16)]. $V_2(0, \gamma, s)$ is a (bending) vibrational potential energy function of γ at small s and vanishes at large $\pm s$. Using arguments in Appendix I, Eq. (13) can be shown to reduce at large $\pm s$ to the sum of the rotational energy of the diatomic and the orbital centrifugal potential of the separated species.

$V_2(\rho, 0, s)$ is a ρ -vibrational potential energy function of ρ at all s . Equation (14) describes the vibrational motion of the ρ coordinate, which is the diatomic's vibration at large $\pm s$ and a symmetric stretching vibration of ABC at small s , as noted earlier. The effective potential for the ρ motion is $V_2(\rho, 0, s) + \alpha_K/\eta^2$; $\eta = 1$ at large $\pm s$. Since α_K is $p_s^2/2\mu$ [cf. Eq. (11)], α_K/η^2 is the kinetic energy of the s motion; it creates an internal centrifugal effect on the ρ motion, as in Part II.

Equations (11), (14), and (16) are the same as those in Part II, except, of course, for the presence of the adiabatic γ, ϕ energy $\epsilon_\gamma(s)$. Equation (13) is first solved for $\epsilon_\gamma(s)$, using the conditions on the γ action variable J_γ described later. Equation (16) then yields $\epsilon_\rho(s)$ which is introduced into (14). Equation (14) is then solved for $\alpha_K(s)$, using the constancy of the vibrational action J_ρ (see later). In an approximate solution of (14) for α_K one might set $\eta \cong 1$ as a zeroth approximation and use perturbation theory to calculate corrections to this α_K .

¹² The square root can be positive or negative, and the customary procedure of letting it mean either is employed at this point.

BOUNDARY CONDITION ON J_γ AT A ROTATIONAL-LIBRATIONAL BOUNDARY

The action variable J_i for any coordinate q^i is defined as $\oint p_i dq^i$, where p_i is the momentum conjugate to q^i and where the integral is over one cycle of motion for q^i . For this definition to be meaningful, there must be some zeroth-order exact or approximate separation of variables, so that p_i can be expressed as a function of q^i . In our case, an adiabatic rather than exact separation was made. It led to Eqs. (13)–(21) and, thus, to expressions for each p_i as a function of its q^i and of s ($q^i \neq s$). One obtains, therefore, meaningful expressions for J_γ and J_ρ . J_ϕ is well defined even in an exact treatment: p_ϕ is a constant of the motion and

$$J_\phi = \oint p_\phi d\phi = 2\pi p_\phi. \quad (22)$$

In (21) a rotational-librational boundary occurs at an s where $E_\gamma(s)$ equals the maximum of $V_2(0, \gamma, s)$. (The maximum is over values of γ .) On one side of this s we have $E_\gamma(s) > V_2(0, \gamma, s)$ for all γ , and the resulting γ motion is rotational, somewhat hindered. On the other side of this s we have $E_\gamma(s) < \max_\gamma V_2(0, \gamma, s)$, and the resulting motion is librational.

Since the adiabatic γ, ϕ energy ϵ_γ is given by (16) and since $V_1(s)$ and $\epsilon_\rho(s)$ are continuous functions of s , $\epsilon_\gamma(s)$ is a continuous function of s , even at any rotational-librational boundary. Thus, the E_γ defined by (19) is also a continuous function of s at that boundary, and, therefore, $E_\gamma - V_2(0, \gamma, s)$ is also a continuous function of s , a fact used in deriving (26) below.

In any s interval which does not include a rotational-librational boundary, J_γ is constant in the adiabatic approximation.^{13,14} Although $\epsilon_\gamma(s)$ is continuous, $J_\gamma(s)$ undergoes an abrupt transition at a rotational-librational boundary, as Eq. (26) derived below shows. At the s which corresponds to a rotational-librational boundary let the entrance to the reaction region lie in a γ interval ($a_1 \leq \gamma \leq a_2$).

Integration of (21) over the interval (a_1, a_2) at any s yields

$$\int_{a_1}^{a_2} p_\gamma d\gamma = p_\phi b \int_{a_1}^{a_2} d\gamma + \int_{a_1}^{a_2} [2I(E_\gamma - V_2^0)]^{1/2} d\gamma, \quad (23)$$

where V_2^0 denotes $V_2(0, \gamma, s)$. On the librational side, $\oint p_\gamma d\gamma$, denoted below by J_γ^l , is twice

$$\int_{a_1}^{a_2} p_\gamma d\gamma$$

and is always positive. The first term on the right side of (23) makes no net contribution to the over-all cycle. Thus,

$$J_\gamma^l = 2 \int_{a_1}^{a_2} [2I(E_\gamma - V_2^0)]^{1/2} d\gamma. \quad (24)$$

On the rotational side $\oint p_\gamma d\gamma$, denoted below by J_γ^r , involves integration over $(0, 2\pi)$, the sign of the square root sign in (25) depending on the sense of the rotation.¹² Thus,

$$J_\gamma^r = 2\pi p_\phi b \pm \int_0^{2\pi} [2I(E_\gamma - V_2^0)]^{1/2} d\gamma. \quad (25)$$

When the entrance channel opening (a_1, a_2) is $(0, 2\pi)$, i.e., when there is only one reaction path, comparison of (24) and (25) and use of (22) and of continuity of $E_\gamma - V_2^0$ shows that

$$J_\gamma^r = 2 |J_\gamma^r - J_\phi b|. \quad (26)$$

A phenomenon analogous to (26) occurred in the quantum-mechanical pendulum problem (in which J_ϕ is zero).¹⁵ The case of two paths is considered in Appendix II.

NONADIABATIC CORRECTIONS

As in a previous section and for simplicity in the present paper, T_1 is neglected and V_2 is approximated by (10); η [given by (9)], r_0 , and R_0 are used to replace η, r , and R in the coefficients in (3). Using the Hamiltonian, $H = T_0 + V$, Hamilton's equations ($\dot{p}_i = -\partial H / \partial q^i$, $\dot{q}^i = \partial H / \partial p_i$) then yield the following results for the ρ, γ and ϕ motions:

$$\begin{aligned} \dot{p}_\rho &= -(\partial / \partial \rho) [V_2(\rho, 0, s) + p_\rho^2 / 2\mu\eta^2], \\ \dot{\rho} &= p_\rho / \mu, \end{aligned} \quad (27)$$

$$\begin{aligned} \dot{p}_\gamma &= -\partial V_2(0, \gamma, s) / \partial \gamma, \\ \dot{\gamma} &= (p_\gamma - p_\phi b) / \mu r_0^2 \lambda, \end{aligned} \quad (28)$$

$$\begin{aligned} \dot{p}_\phi &= 0, \\ \dot{\phi} &= (p_\phi - F p_\gamma) / \mu R_0^2 \lambda. \end{aligned} \quad (29)$$

After introducing as an approximation the adiabatic value for $s(t)$ and $p_s(t)$ on the right side of each of these pairs of equations, each pair can be integrated, thus yielding an approximate nonadiabatic solution to the specified problem.

More instructive physically is the approximate integration (or reduction to quadratures) of Eqs. (27)–(29) by analytical methods. A Hamilton–

¹³ M. Born, *The Mechanics of the Atom* (Frederick Ungar Publ. Co., New York, 1960), Chap. 2.

¹⁴ The proof of adiabatic invariance applies, as one may see from the actual derivation in Ref. 13, only to a region which does not include a rotational-librational boundary. At such a boundary, we show in (26), an abrupt jump occurs in J_γ , though not in J_ρ or J_ϕ . The character of only the γ motion changes at such a boundary.

¹⁵ In this pendulum problem [E. U. Condon, Phys. Rev. 31, 891 (1928)] the principal quantum number increases by a factor of about two in an adiabatic correlation in which the rotational motion becomes librational; e.g., cosine rotational wavefunctions for $j=0, \pm 1, \pm 2, \dots$ correlate with even vibrational wavefunctions ($v=0, 2, 4, \dots$) and sine rotational wavefunctions for $j=0, \pm 1, \pm 2, \dots$ correlate with odd vibrational wavefunctions ($v=1, 3, 5, \dots$). At high enough quantum numbers one obtains $v=2|j|$.

Jacobi¹³ treatment is used below to integrate these equations using the adiabatic value for $s(t)$. The advantage of using angle-action variables is that the action variables J_i are adiabatic invariants.^{13,14}

Equations (27)–(29) are also Hamilton's equations, $\dot{p}_i = -\partial\mathcal{H}/\partial q^i$, $\dot{q}^i = \partial\mathcal{H}/\partial p_i$, in which the Hamiltonian $\mathcal{H}$, given by (30), contains s as a time-dependent parameter. This s is the adiabatic $s(t)$ and the q^i are γ , ϕ and ρ ; p_i is conjugate to q^i ,

$$\mathcal{H}(q^i, p_i, s) = \frac{p_\gamma^2}{2\mu r_0^2} + \frac{(p_\phi - F p_\gamma)^2}{2\mu R_0^2 \lambda} + V_2(0, \gamma, s) + \frac{p_\rho^2}{2\mu} + V_2(\rho, 0, s) + \frac{\alpha_K(s)}{\eta^2}. \quad (30)$$

The Hamilton–Jacobi equation at each s , obtained from (30) by replacing p_i by $\partial W/\partial q^i$, is

$$\mathcal{H}(q^i, \partial W/\partial q^i, s) = E - V_1(s), \quad (31)$$

Comparison with (12)–(14) and (16) shows that (31) is satisfied by the adiabatic solution for the γ , ϕ , and ρ motions and that this W , which is the one used in the remainder of this paper, is the same as $W_2 + p_\phi \phi$. [It differs from the W in (6).] W can be regarded as a function of (q^i, J_i, s) , where J_i denotes $\oint p_i dq^i$ at that s . If w_i is the angle variable canonically conjugate to J_i , the transformation from (q^i, p_i) to (J_i, w_i) is given by

$$p_i = \partial W/\partial q^i, \quad w_i = \partial W/\partial J_i \quad (q^i = \gamma, \phi, \rho). \quad (32)$$

When $\mathcal{H}$ is expressed in terms of the w_i and J_i they satisfy Hamilton's equations,

$$\dot{J}_i = -\partial\mathcal{H}/\partial w_i = 0, \quad \dot{w}_i = \partial\mathcal{H}/\partial J_i \quad (\text{fixed } s). \quad (33)$$

Integration of the last result at any s yields

$$w_i = \nu_i t + \delta_i \text{ at any } s \quad (\text{fixed } s), \quad (34)$$

where $\nu_i(s)$ is the local frequency¹³ of the q^i motion and δ_i is constant,

$$\nu_i(s) = \partial\mathcal{H}/\partial J_i. \quad (35)$$

After solving (31) for J_i and w_i at each s , the non-adiabatic correction can be obtained by replacing s in $\mathcal{H}$ by its adiabatic value $s(t)$. (The nonadiabatic correction for J_ϕ is zero.¹⁶) The canonical transformation from (q^i, p_i) to (w_i, J_i) , when s is replaced by $s(t)$, transforms $\mathcal{H}$ to $\tilde{\mathcal{H}}$, given by (36). The variables J_i and w_i satisfy (38) and (39),¹³

$$\tilde{\mathcal{H}}[w_i, J_i, s(t)] = \mathcal{H}[q^i, p_i, s(t)] + \partial W^*/\partial t, \quad (36)$$

where

$$W^*(q^i, w_i, s) = W - \sum_i J_i w_i, \quad (37)$$

$$J_i = -\partial\mathcal{H}/\partial w_i, \quad (38)$$

$$\dot{w}_i = \partial\mathcal{H}/\partial J_i. \quad (39)$$

¹³ That is, the subsequent approximations do not upset angular momentum conservation: e.g., Eqs. (66) and (73) for $\partial W^*/\partial t$ do not depend on w_ϕ .

In (36) $\mathcal{H}(q^i, p_i, s)$ is first expressed in terms of (J_i, w_i, s) . This $\mathcal{H}$ is independent of w_i . One then finds¹³

$$\dot{J}_i = -(\partial/\partial w_i)(\partial W^*/\partial t), \quad (40)$$

$$\dot{w}_i = (\partial\mathcal{H}/\partial J_i) + (\partial/\partial J_i)(\partial W^*/\partial t). \quad (41)$$

In these equations W^* is first expressed in terms of all q 's, w 's, and t and the q 's and w 's are held constant in computing $\partial W^*/\partial t$. $\partial W^*/\partial t$ is then expressed in terms of all J 's, w 's, and t , and in the final differentiations in (40) and (41) all variables but w_i and J_i , respectively, are held constant.¹³

These equations provide the nonadiabatic correction to $\dot{J}_i$ (and to $\dot{w}_i$). Use of the leading term on the right side of (41), when permissible, followed by integration yields

$$w_i = \int_{t_0}^t \nu_i(s) dt + \delta_i, \quad (42)$$

where δ_i is the phase of w_i at some time t_0 and where the adiabatic solution $s(t)$ is introduced for the argument s .

J_ϕ is, of course, a constant of the motion. In the adiabatic case J_γ is constant, except for a jump at each librational-rotational boundary described earlier, and J_ρ is a constant for all s .

A SPECIFIC EXAMPLE

A specific example of the above treatment is considered in this section. $V_2(0, \gamma, s)$ is periodic in γ , with period 2π , or in some cases $2\pi/n$. It can be expanded in a Fourier series, the first two terms of which are given by (43) when the γ barrier has a minimum at $\gamma=0$. The case of $n=2$ is given in Appendix II,

$$V_2(0, \gamma, s) = \frac{1}{2}(1 - \cos\gamma)A(s), \quad (43)$$

where the γ barrier $A(s)$ vanishes at large $\pm s$. More complicated Fourier expansions than the above can also be treated. Using the first half of (32), W is

$$W = p_\phi \phi + \int p_\gamma d\gamma + \int p_\rho d\rho. \quad (44)$$

Equations (21), (22), and (44) yield

$$W(q^i, J_i, s) = \frac{J_\phi}{2\pi}(\phi + b\gamma) + \left(\frac{2IA}{k^2}\right)^{1/2} \times \int (1 - k^2 \sin^2 \frac{1}{2}\gamma)^{1/2} d\gamma + \int p_\rho d\rho, \quad (45)$$

where the last term [denoted in (12) by W_3] is expressed in terms of (ρ, J_ρ, s) later; k^2 is a reduced γ barrier,

$$k^2 = A/E_\gamma. \quad (46)$$

k is determined as a function of J_γ and J_ϕ in the following sections.

The expression (30) for $\mathcal{H}$ can be written as follows,

upon using (13), (14), (19), and (46):

$$\mathcal{H} = (A/k^2) + (J_\phi^2/8\pi^2\mu R_0^2) + \epsilon_p, \quad (47)$$

where ϵ_p is expressed in terms of J_ϕ .

There are different intervals of s to be considered: (i) intervals of s in which the γ motion is rotational (i.e., $k < 1$), and (ii) an interval of s in which the γ motion is librational ($k > 1$). The condition on J_γ at a boundary of these two intervals is given by (26).

A. Adiabatic Treatment

Case (i): s Interval for which Motion is Rotational ($k < 1$)

Since J_γ equals $\oint p_\gamma d\gamma$, it equals the change in W during one cycle of the periodic γ motion. For a rotational motion, it therefore equals twice the change of W during the first half cycle. During the latter γ varies from 0 to π . Equation (45) therefore yields¹⁷

$$J_\gamma = 2 \left(\frac{2IA}{k^2} \right)^{1/2} \int_0^\pi (1 - k^2 \sin^2 \frac{1}{2}\gamma)^{1/2} d\gamma + J_\phi b. \quad (48)$$

There are two cases to consider: The square root sign, and therefore $J_\gamma - J_\phi b$, can be positive or negative. We consider the positive sign first and then give the changes to be made when the sign is negative.

At any given s and J_ϕ , J_γ depends only on k . Since w_γ is $(\partial W/\partial J_\gamma)_{\gamma,s}$ it equals

$$\frac{(\partial W/\partial k)_{\gamma,s}}{(\partial J_\gamma/\partial k)_{\gamma,s}}$$

and is found to be

$$w_\gamma = \int (1 - k^2 \sin^2 \frac{1}{2}\gamma)^{-1/2} d\gamma / 2 \times \int_0^\pi (1 - k^2 \sin^2 \frac{1}{2}\gamma)^{-1/2} d\gamma. \quad (49)$$

Using the usual notation of elliptic integrals,^{18,19} the latter equations become

$$J_\gamma - J_\phi b = 4(2IA/k^2)^{1/2} E(k), \quad (50)$$

$$w_\gamma = F(\frac{1}{2}\gamma, k)/2K(k), \quad (51)$$

where $F(\frac{1}{2}\gamma, k)$ and $E(\frac{1}{2}\gamma, k)$ are normal elliptic integrals of the first and second kind, and where $K(k)$ and $E(k)$ are the corresponding complete integrals [$=F(\frac{1}{2}\pi, k)$, $E(\frac{1}{2}\pi, k)$, respectively]. In (51) the right side increases by unity when γ changes by 2π .

¹⁷ The sign of the variables J_i and w_i throughout are chosen in accordance with the remarks in Ref. 13, p. 45. Thereby, $J_\gamma - J_\phi b$ in (48) can be positive or negative,¹⁸ but J_γ in (56) is positive. The variable w_γ in each case is to be defined in a way that it increases monotonically with time, namely increases by +1 during one period of the motion.

¹⁸ P. F. Byrd and M. D. Friedman, *Handbook of Elliptic Integrals for Engineers and Physicists* (Springer-Verlag, Berlin, 1954).

¹⁹ According to (49) w_γ is an odd function of γ (e.g., as seen by changing to $-\gamma$, etc., or by expanding in a power series in k^2 and integrating termwise). Thus, $w_\gamma = 0$ at $\gamma = 0$, a result used in re-writing (49) as (51). The same remarks apply to (57).

Equation (51) only describes the relation between w_γ and γ . At any fixed s the dependence of w_γ on time t is (34), where the frequency of the γ motion is found from $\partial\mathcal{H}/\partial J_\gamma$ to be

$$\nu_\gamma = (J_\gamma - J_\phi b)/16KEI. \quad (52)$$

The last three expressions reduce to the standard ones for a rotator²⁰ when A (the γ barrier) and b are set equal to zero.

When $J_\gamma - J_\phi b$ is negative the right hand sides of (50)–(52) should be multiplied by -1 .¹⁷ We note that $J_\gamma - J_\phi b$ does not change sign during motion in the given s interval, since Eqs. (46) and (50) show that $J_\gamma - J_\phi b \neq 0$. [They do not have a solution for k in the interval ($0 \leq k < 1$) when $J_\gamma - J_\phi b = 0$.]

w_ϕ is obtained from (32) and (45). In differentiating the second term in the right hand side of (45) we note that $\partial/\partial J_\phi$ is

$$\frac{\partial/\partial k}{\partial J_\phi/\partial k}.$$

One finds

$$w_\phi = [(\phi + b\gamma)/2\pi] - [bF(\frac{1}{2}\gamma, k)/2K(k)]. \quad (53)$$

Equations (51) and (53) yield

$$w_\phi = [(\phi + b\gamma)/2\pi] - bw_\gamma. \quad (54)$$

At large $\pm s$, k is negligible. Then, the last term in (53) reduces to $b\gamma/2\pi$ and w_ϕ becomes $\phi/2\pi$.

Case (ii): s Interval for which Motion is librational ($k > 1$)

J_γ again equals the increase in W during one cycle of the periodic motion. For a librational motion the $J_\phi b\gamma/2\pi$ term in (45) is seen, therefore, to make no contribution to J_γ , while the contribution of the next term is four times its contribution during the first quarter-cycle. At any s let the maximum value of $|\gamma|$ be $\gamma_0(s)$. Then

$$1 - k^2 \sin^2 \frac{1}{2}\gamma_0 = 0. \quad (55)$$

We have

$$J_\gamma = 4 \left(\frac{2IA}{k^2} \right)^{1/2} \int_0^{\gamma_0} (1 - k^2 \sin^2 \frac{1}{2}\gamma)^{1/2} d\gamma. \quad (56)$$

As before, at any given s , J_γ depends only on k .

Instead of (49) one now obtains

$$w_\gamma = \int (1 - k^2 \sin^2 \frac{1}{2}\gamma)^{-1/2} d\gamma / 4 \times \int_0^{\gamma_0} (1 - k^2 \sin^2 \frac{1}{2}\gamma)^{-1/2} d\gamma. \quad (57)$$

²⁰ $J_\gamma = (8\pi^2 I E_\gamma)^{1/2}$ (more familiar as $E_\gamma = J_\gamma^2/8\pi^2 I$), $w_\gamma = \gamma/2\pi$, $\nu_\gamma = J_\gamma/4\pi^2 I$. (Compare Ref. 13, p. 63).

In terms of elliptic integrals we have²¹

$$J_\gamma = 8(2IA/k^2)^{1/2} E(\frac{1}{2}\gamma_0, k), \quad (58)$$

$$w_\gamma = F(\frac{1}{2}\gamma, k)/4F(\frac{1}{2}\gamma_0, k). \quad (59)$$

As before, w_γ depends on time according to (34), but now²¹

$$\nu_\gamma = \frac{(A/2I)^{1/2}}{4kF(\frac{1}{2}\gamma_0, k)}. \quad (60)$$

Now $k > 1$, and it is customary to express the elliptic integrals and functions in terms of a modulus ($k_1 = 1/k$) which is less than unity. Introduction of the usual transformations²² yields

$$J_\gamma = 8(2IA)^{1/2} k_1^2 (K_1 - D_1), \quad (61)$$

$$w_\gamma = F(\beta, k_1)/4K_1, \quad (62)$$

$$\nu_\gamma = \frac{(A/2I)^{1/2}}{4K_1}, \quad (63)$$

where β is defined by $\sin\beta = k \sin\frac{1}{2}\gamma_0$. K_1 denotes $K(k_1)$, and D_1 denotes $[K(k_1) - E(k_1)]/k_1^2$.

The last three equations reduce to the standard one for a vibrator when the barrier is made high, i.e., when k_1 is made small.²³

The expression obtained for w_ϕ is obtained in a way analogous to that in the previous section, but now k does not depend on J_ϕ . Thereby,

$$w_\phi = (\phi + b\gamma)/2\pi. \quad (64)$$

At small s , where $F \approx 0$, w_ϕ is seen to equal $\phi/2\pi$. Equation (64) is continuous with (53) at $k=1$, since $K(1) = \infty$.

B. Nonadiabatic Correction

(i) s Intervals where $k < 1$

The nonadiabatic correction is obtained by first computing W^* . We first consider the case where $J_\gamma - J_\phi b$ is positive in the cited s interval. Equations (37), (45), (50), and (54) yield

$$W^*(q, w, t) = \left(\frac{2B}{k^2}\right)^{1/2} \times \left(\int (1 - k^2 \sin^2 \frac{1}{2}\gamma)^{1/2} d\gamma - 4E(k)w_\gamma \right) + W_3^*, \quad (65)$$

²¹ Derivatives of the elliptic integrals and functions are given in Ref. 18, p. 282ff.

²² Reference 18, pp. 38 and 39.

²³ That is, they reduce to

$$\begin{aligned} J_\gamma &= E_\gamma/\nu_\gamma, \\ 2\pi w_\gamma &= \sin^{-1}[(4\pi^2 I \nu_\gamma / 2J_\gamma)^{1/2} \gamma], \\ \nu_\gamma &= (A/2I)^{1/2}/2\pi; \end{aligned}$$

$A/2$ is the force constant when E_γ/A is small. At small k_1 , $F(\beta, k_1) \approx \beta$ and the limiting values of the other elliptic functions and integrals are given in Ref. 18, p. 11. Derivation of the usual harmonic oscillator expressions may be found in Ref. 13, pp. 51 and 52.

where k is to be expressed in terms of w_γ and γ using (51) and $W_3^*(\rho, w_\rho, t)$ is $W_3 - J_\rho w_\rho$. Hence,

$$\begin{aligned} \frac{\partial W^*}{\partial t} &= (2k^2 B)^{-1/2} \dot{B} \\ &\times \left(\int (1 - k^2 \sin^2 \frac{1}{2}\gamma)^{1/2} d\gamma - 4E(k)w_\gamma \right) + \frac{\partial W_3^*}{\partial t} \quad (66) \end{aligned}$$

where

$$B = AI \quad (67)$$

and where the dot denotes d/dt ; $\partial W_3^*/\partial t$ depends only on J_ρ and w_ρ . We return to it in a later section. Use was made of the fact, evident from (51), that k is constant when both γ and w_γ are constant.

Equation (40) and introduction of the Jacobian zeta function $Z(u)$,²⁴ which can be approximated by trigonometric functions if desired, now yields

$$\dot{J}_\gamma = -[16EK/(J_\gamma - J_\phi b)k^2][\dot{B}dZ(u)/du], \quad (68)$$

where u is $2Kw_\gamma$. The right side of (68) never becomes singular since, as noted earlier, $J_\gamma - J_\phi b \neq 0$ when ($0 \leq k < 1$).

Equation (68) can be regarded as a first-order nonlinear equation with J_γ and t as variables, and can be integrated numerically.^{25,26} [k^2 depends on $(J_\gamma - J_\phi b)^2$ and s , as in (50); w_γ depends on t as in (42), in the first approximation.] A more approximate procedure, one which is quite logical in view of the choice of the adiabatic solution as the zeroth-order one, is the following.

The right side of (68) is periodic in w_γ . When B varies slowly enough the integral of the right side vanishes and one obtains adiabatic invariance of J_γ .²⁷ In the first approximation, therefore, J_γ may be replaced by its value at the time (t_0) at the start of this s interval, J_γ^0 . With this substitution k still varies with s , according to (50), because of its dependence on b and on IA (i.e., on B). Each s on the right side of (68) is replaced by the adiabatic $s(t)$. Integration yields

$$J_\gamma - J_\gamma^0 = -16 \int_{t_0}^t \frac{EK}{(J_\gamma^0 - J_\phi b)k^2} \dot{B} \frac{dZ}{du} dt. \quad (69)$$

²⁴ Reference 18, pp. 33, 34, and 300.

²⁵ It should be noted that at $k=1$, w_γ is not a suitable variable, since $\nu_\gamma=0$ there. The relation between γ and t is unaffected, however, since the offending $K(k)$ cancels when (34), (51), and (52) are combined before letting $k \rightarrow 1$. [$K(1) = \infty$.] [However, if the immediate neighborhood of $k=1$ makes only a minor contribution to the integration of (68) and (75), w_γ need not be transformed to γ in this neighborhood.] An alternative which we hope to explore is the transformation of (J_γ, w_γ) into other variables, particularly near $k=1$, just as it is convenient later for certain purposes to transform (J_ρ, w_ρ) into (a, a^*) via (90).

²⁶ In the first approximation the w_γ present in u in (68), u_0 in (74), and u_1 in (75) obeys Eq. (42). In the next approximation the influence on w_γ of the $\partial W^*/\partial t$ term in (41) must be included.

²⁷ The proof would be analogous to that employed in Ref. 13, §10, §14.

The region near the top of the barrier ($E_\gamma = A$, i.e., $k \approx 1$) is more complicated dynamically than the region where E_γ is appreciably larger than A (i.e., k small), and we obtain an approximate, simple formula for the latter region as follows.

In a Fourier expansion²⁴ of $(K/k^2)(dZ/du)$ the coefficients depend on k^2 . Only the leading term $(\pi/4) \cos 2\pi w_\gamma$ need be considered when k is small, and one obtains

$$J_\gamma - J_\gamma^0 \cong -4\pi \int_{t_0}^t \frac{E\dot{B}}{(J_\gamma^0 - J_\phi b)} \cos 2\pi w_\gamma dt. \quad (70)$$

Because of the relatively low frequency of the rotational motion one may expect an appreciable rotational nonadiabaticity.

Regardless of whether or not k is small the γ , ϕ energy $\epsilon_\gamma(s)$ is obtained from (19), (26), (46) and (50),

$$\epsilon_\gamma = [(J_\gamma - bJ_\phi)^2/32E^2I] + [J_\phi^2/8\pi^2\mu R_0^2]. \quad (71)$$

When $J_\gamma - J_\phi b$ is negative the right hand sides of (65) and (66) are to be multiplied by -1 . $Z(u)$ depends on k^2 and is an even function of u . Equation (50) shows that k^2 is an even function of $J_\gamma - J_\phi b$. Thus, $(EK/k^2)dZ/du$ is unaffected when (50) and (51) are multiplied by -1 . Examination of the details of the derivation leading to (68) or, more simply, use of physical symmetry, shows that Eq. (68) applies when $J_\gamma - J_\phi b$ is negative also.

(ii) *s* Intervals where $k > 1$

W^* , obtained from (37), (45), (58), and (64), is

$$W^* = \left(\frac{2B}{k^2}\right)^{1/2} \times \left(\int (1 - k^2 \sin^2 \frac{1}{2}\gamma)^{1/2} d\gamma - 8E(\frac{1}{2}\gamma_0, k)w_\gamma \right) + W_3^* \quad (72)$$

and $\partial W^*/\partial t$ is, therefore,

$$\left(\frac{\partial W^*}{\partial t}\right)_{\phi, w_\gamma} = (2k^2 B)^{-1/2} \dot{B} \times \left(\int (1 - k^2 \sin^2 \frac{1}{2}\gamma)^{1/2} d\gamma - 8E(\frac{1}{2}\gamma_0, k)w_\gamma \right) + \frac{\partial W_3^*}{\partial t}. \quad (73)$$

(As before, k and thereby γ_0 are constant when both γ and w_γ are constant.) k is constant at constant J_γ and B , as one sees from (55) and (58). Equation (40)

now yields

$$\dot{J}_\gamma = 8(1/2B)^{1/2}(\dot{B}/k)[E(\frac{1}{2}\gamma_0, k) - F(\frac{1}{2}\gamma_0, k)dn^2u_0], \quad (74)$$

where $u_0 = 4w_\gamma F(\frac{1}{2}\gamma_0, k)$. As before, elliptic functions and integrals are next expressed in terms of those with a modulus $k_1 (= 1/k)$ which is less than unity. After the introduction of the Jacobian zeta function one finds

$$\dot{J}_\gamma = -8(1/2B)^{1/2}(\dot{B}K_1)[dZ(u_1)/du_1], \quad (75)$$

where u_1 is $4w_\gamma K_1$ and the modulus in $Z(u_1)$ is k_1 . Equation (75) can be regarded as a first-order non-linear equation in J_γ and t and integrated numerically. However, when the zeroth-order (adiabatic) approximation is introduced for J_γ on the right hand side, (76) given below is obtained as follows.

We note that the right side of (75) is a periodic function of w_γ and vanishes on integration when B varies slowly enough.²⁷ If the value of J_γ at the start of the interval ($t = t_0$) is J_γ^0 , J_γ^0 is introduced for J_γ in each k_1 (and in each function of k_1) in (75). Integration yields

$$J_\gamma - J_\gamma^0 = - \int_{t_0}^t 8(2B)^{-1/2}(\dot{B}K_1) \frac{dZ(u_1)}{du_1} dt. \quad (76)$$

The region near the bottom of the barrier (i.e., $E_\gamma \ll A$, or $k_1 \ll 1$) is simpler dynamically than near the top of the barrier. When $(K_1/k_1^2)dZ(u_1)/du_1$ is expanded in a Fourier series,²⁴ only the leading term need be considered at low k_1 and one obtains

$$J_\gamma - J_\gamma^0 \cong -2\pi k_1^2 \int_{t_0}^t (2B)^{-1/2} \dot{B} \cos 4\pi w_\gamma dt. \quad (77)$$

The tendency for J_γ to change is seen to depend on the change of barrier during the bending vibrational period.

The total change in J_γ from its initial value at $s = -\infty$ to any other s , i.e., to any stage of the reaction, is obtained by adding the contributions of the distinct s intervals, after applying the condition (26) at the boundary of two intervals.

THE VIBRATIONAL ρ -MOTION

In the previous section the γ , ϕ motions were considered, together with the effect of the s motion on them. We turn now to the behavior of the ρ coordinate. For a specific example we expand the effective potential energy function for the ρ motion quadratically, after defining U , ρ_0 , and an effective frequency ω ,

$$U(\rho, s) = V_2(\rho, 0, s) + \alpha_K(s)/\eta^2, \quad (78)$$

$$\partial U(\rho_0, s)/\partial \rho_0 = 0, \quad (79)$$

$$\mu\omega^2 = \partial^2 U(\rho_0, s)/\partial \rho_0^2. \quad (80)$$

The adiabatic Eq. (14) now reads

$$(2\mu)^{-1}(dW_3/d\rho)^2 + \frac{1}{2}\mu\omega^2(\rho - \rho_0)^2 = \epsilon(s), \quad (81)$$

where

$$\epsilon = \epsilon_p - U(\rho_0, s). \quad (82)$$

According to (78) $U(\rho_0, s)$ is the sum of the extra barrier, $V_2(\rho_0, 0, s)$, and of the s kinetic energy at $\rho = \rho_0$.

Integration of (81) yields the well-known value of the generating function W_3 , from which one can then compute W_3^* , the contribution of $W_3 - J_p w_p$ to W^* . This W_3^* is found to be²⁸

$$W_3^*(\rho, w_p, s) = \frac{1}{2}\mu\omega(\rho - \rho_0)^2 \cot 2\pi w_p. \quad (83)$$

$\rho - \rho_0$ is found to be²⁸

$$\rho - \rho_0 = (J_p/\mu\omega\pi)^{1/2} \sin 2\pi w_p, \quad (84)$$

and $\partial W_3^*/\partial t$, obtained from (83), is

$$(\partial W_3^*/\partial t)_{\rho, w_p} = \mu(\rho - \rho_0) \left[\frac{1}{2}(\rho - \rho_0)\dot{\omega} - \omega\dot{\rho}_0 \right] \cot 2\pi w_p. \quad (85)$$

When $\partial W_3^*/\partial t$ is expressed in terms of J_p and w_p using (84), Eqs. (40) and (41) yield

$$\dot{J}_p = -2\dot{\rho}_0(\mu\omega\pi J_p)^{1/2} \sin 2\pi w_p - (J_p\dot{\omega}/\omega) \cos 4\pi w_p, \quad (86)$$

$$\dot{w}_p = (\omega/2\pi) - \frac{1}{2}\dot{\rho}_0(\mu\omega/J_p\pi)^{1/2} \cos 2\pi w_p + (\dot{\omega}/4\pi\omega) \sin 4\pi w_p. \quad (87)$$

When the initial action J_p^0 is not too small, the second of these equations does not become singular (see later). After setting J_p equal to J_p^0 in the right hand side of first equation, because of the near-adiabatic condition, integration yields

$$J_p \cong J_p^0 - (2J_p^0)^{1/2} \int_{-\infty}^t \dot{\rho}_0(\mu\omega\pi)^{1/2} \sin 2\pi w_p dt' - J_p^0 \int_{-\infty}^t \frac{\dot{\omega}}{\omega} \cos 4\pi w_p dt', \quad (88)$$

where, when only the first term in (87) need be considered,

$$2\pi w_p = \int_{t_0}^{t'} \omega dt'' + \delta_p. \quad (89)$$

δ_p is the value of the phase $2\pi w_p$ at any time t_0 .

However, a transformation must be introduced to integrate (86) and (87) if J_p^0 is too small, since the coefficient of $\dot{\rho}_0$ in (87) is singular at $J_p = 0$. We define

a variable a and its complex conjugate a^* ,

$$a = J_p^{1/2} \exp(-2\pi i w_p). \quad (90)$$

In terms of a and a^* , Eqs. (86) and (87) become

$$\dot{a} = -i\omega a + i\dot{\rho}_0(\mu\omega\pi)^{1/2} - (\dot{\omega}a^*/2\omega) \quad (91)$$

and $\dot{a}^*$ is given by the complex conjugate of this equation. The first term on the right hand side of (91) is the adiabatic term, and the $\dot{\rho}_0$ term reflects the non-adiabatic effect due to the curvature of Curve C. When the last term is temporarily omitted, integration of (91) yields²⁹

$$a = a_0 \exp \left(-i \int_{t_0}^t \omega dt \right) + i \int_{t_0}^t \left[\dot{\rho}_0(\mu\omega\pi)^{1/2} \exp \left(i \int_{t_0}^{t'} \omega dt'' \right) \right] dt, \quad (92)$$

where a_0 is the value of a at time t_0 . When t_0 is chosen to occur at large negative s , the t_0 in the integral involving $\dot{\rho}_0$ can be replaced by $-\infty$. The action J_p is seen from (90) to equal aa^* . Thereby,

$$J_p = J_p^0 - (2J_p^0)^{1/2} \int_{-\infty}^t \left[\dot{\rho}_0(\mu\omega\pi)^{1/2} \times \sin \left(\int_{t_0}^{t'} \omega dt'' + \delta_p \right) \right] dt' + \left| \int_{-\infty}^t \left[\dot{\rho}_0(\mu\omega\pi)^{1/2} \times \exp \left(i \int_{t_0}^{t'} \omega dt'' \right) \right] dt' \right|^2. \quad (93)$$

Equation (93) is of course more general than (88), apart from the $\dot{\omega}$ term. The first two terms on the right hand side of both equations are the same. The last term in (93) is independent of J_p^0 and of δ_p . Comparison³⁰ with the various expressions of Part II shows them to be the same (except for the omitted $\dot{\omega}$ terms).

When the adiabatic term for a^* ,

$$a_0^* \exp \left(i \int_{t_0}^t \omega dt \right),$$

is introduced into (91), the leading additional contribution to the right side of (93) is Δ .

$$\Delta = -J_p^0 \int_{-\infty}^t \frac{\dot{\omega}}{\omega} \cos 2 \left(\int_{t_0}^{t'} \omega dt'' + \delta_p \right) dt', \quad (94)$$

which is the same as the last term in (88).

²⁸ The largest contribution to ΔJ_p is usually expected to arise from the curvature of Curve C rather than from $\dot{\omega}$, the variation in effective frequency. When the reverse is true, a different approximation scheme can be formulated.

²⁹ The comparison is most easily made by comparing the present Eqs. (84) and (93) with Eq. (29) of Part II and integrating the latter once by parts. One first obtains $\rho - \rho_0 = (a^* - a)/2i(\mu\omega\pi)^{1/2}$ from (84) and (90) then introduces (92).

³⁰ Reference 10, pp. 190 and 191

At any s the ρ vibrational energy ϵ is related to J_ρ by²⁸

$$\epsilon = J_\rho \omega / 2\pi. \quad (95)$$

ANGULAR DISTRIBUTION

The angular distribution is obtained from the behavior of the angle variable w_ϕ , which obeys (53) and (64) for $k < 1$ and $k > 1$, respectively. The boundary condition on w_ϕ at the rotational-librational boundary (i.e., at $k = 1$) is seen from (53) and (64) that w_ϕ be continuous, since the last term in (53) vanishes, except at $\gamma = \pm\pi$. [$K(1) = \infty$].

According to (41), (47), (66), and (73) w_ϕ is given by

$$\begin{aligned} (k < 1) \quad w_\phi &= (J_\phi / 4\pi^2 \mu R_0^2) - \nu_\gamma b + w_\phi', \\ (k > 1) \quad w_\phi &= (J_\phi / 4\pi^2 \mu R_0^2), \end{aligned} \quad (96)$$

where ν_γ is given by (52) and where w_ϕ' is the contribution from $\partial[\partial W^* / \partial t] / \partial J_\phi$. In deriving (96) we used (50) to show that $(\partial k / \partial J_\phi) = -b \partial k / \partial J_\gamma$ when $k < 1$.

At large $\pm s$, ϕ becomes constant. If ϕ^0 and ϕ^∞ denote the initial and final values of ϕ and if w_ϕ' is neglected one finds from the above results

$$\phi^\infty - \phi^0 = \int_{-\infty}^{\infty} g dt \quad (97)$$

where the integrand g is

$$\begin{aligned} g &= J_\phi / 2\pi \mu R_0^2 \quad (k > 1), \\ g &= (J_\phi / 2\pi \mu R_0^2) - 2\pi b \nu_\gamma \quad (k < 1). \end{aligned} \quad (98)$$

Since $\nu_\gamma = 0$ at $k = 1$, g is a continuous function of s . The integrand has its expected value at small and large $\pm s$: At small s and, hence, in the region $k > 1$ the total angular momentum determines changes in ϕ , via $\mu R_0^2 \dot{\phi} = p_\phi = J_\phi / 2\pi$; μR_0^2 is the relevant moment of inertia (Appendix I). At large $\pm s$, and hence, in the region of $k < 1$, g in (98) can be shown to reduce to $(J_\phi - FJ_\gamma) / 2\pi \mu (R_0^2 - r_0^2)$. Since $(J_\phi - FJ_\gamma) / 2\pi$ and $\mu(R_0^2 - r_0^2)$ equal the orbital angular momentum and orbital moment of inertia at large $\pm s$ (Appendix I), we have $\mu(R_0^2 - r_0^2) \dot{\phi} = (J_\phi - FJ_\gamma) / 2\pi$ in that region, and so the integrand there is the expected one.

It is noted that g provides a smooth interpolation between these expected values.

PROBABILITY OF REACTION

We consider the adiabatic system first. For any given set of initial J_i 's reaction occurs when the solution of (11)–(16) yields an $\alpha_K(s)$ which is positive at all s , i.e., a p_s which is nowhere imaginary. (In the adiabatic case this solution is independent of the δ_i 's.) Thus, reaction occurs when, for all s ,

$$E \geq V_1(s) + \epsilon_\gamma(s) + \epsilon(s) + V_2(\rho_0, 0, s), \quad (99)$$

as can be seen from (16), (78), and (82). In order of appearance, these terms represent the natural barrier on Curve C, the γ , ϕ energy, the ρ energy, and the potential energy increment from Curve C ($\rho = 0$) to $\rho = \rho_0$, i.e., to the point where the ρ potential is a minimum. The centrifugal effects are included in ϵ_γ , of course. E equals $\alpha_K^0 + \epsilon_\gamma^0 + \epsilon^0$, where the 0 's denote initial values. α_K^0 is the initial energy of relative translational motion of the reactants. The effective barrier is the smallest α_K^0 for which (99) is fulfilled. It depends on all J_i 's, since $\epsilon_\gamma(s)$ depends on J_ϕ and J_γ^0 and $\epsilon(s)$ depends on J_ρ^0 . For example, a large impact parameter leads to a large J_ϕ (unless cancelled by a large J_γ^0) and thereby leads both to a large centrifugal potential and, also, to a large J_γ in the small s region because of (26). In contrast, a large J_ρ^0 usually lowers the effective barrier; ω at small s is usually less than that at $s = -\infty$ and so, according to (95), $\epsilon(s) - \epsilon^0(s)$ is usually negative when $J_\rho(s)$ is roughly constant.

In the nonadiabatic case ϵ_γ at small s is obtained from J_γ and J_ϕ at that s using (71); ϵ is obtained from J_ρ using (95). These J_i 's are found by integration of (68), (75), and (93). Thus, once again, the right side of (99) can be calculated for any E and δ_i 's to see when reaction occurs. The difference of both sides of (99) is the value of α_K / η^2 at $\rho = \rho_0$, according to (16), (78), and (82). An iterative scheme can be set up to calculate this quantity and so improve on the adiabatic result for it. When a system has an α_K / η^2 which is everywhere positive even if the adiabatic α_K / η^2 is not, the system can be said to undergo a nonadiabatic leak.²⁹

For any given initial J_i 's and initial $p_s^2 / 2\mu$ the reaction probability can now be computed from the above results, using a uniform distribution in the initial δ_i 's.

ADIABATIC CORRELATION

We consider here the adiabatic correlation for the ϕ , ρ , and γ motions. The simplest adiabatic correlation involves J_ϕ . J_ϕ is a constant because the total angular momentum $p_\phi (= J_\phi / 2\pi)$ is a constant of the motion.

The following pattern for adiabatic correlation occurs for the ρ motion. When the initial s energy is adequate a reactive collision occurs. A diatomic reactant in state v (value of the vibrational action $\oint p_\rho d\rho$) yields an ABC system whose local symmetric stretching vibration at small s is in state v , and then yields a diatomic product in state v . When the initial s energy is not adequate, the reflection occurs and the diatomic reactant is reformed in state v . ABC systems at the top of the barrier for the s motion, i.e., at the maximum of the right side of (99), are the "activated complexes."³¹

In considering the adiabatic correlation for the

²⁸ Compare R. A. Marcus, J. Chem. Phys. 45, 2138 (1966); 43, 1598 (1965).

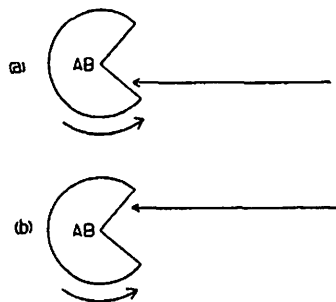


FIG. 2. Pictorial diagram for boundary condition (26). Collision (a) is a harder collision (leads to a more highly excited A...B...C bending vibration) than collision (b).³²

γ motion, we first note that the angular momentum of the diatomic reactant (product) at large $\pm s$ equals $FJ_\gamma/2\pi$ (Appendix I). When the initial s energy is adequate the γ differential equation reveals that a diatomic reactant initially having a rotational angular momentum j forms an ABC system whose local bending vibration is in a state given by the boundary condition (26), where $J_\gamma/2\pi$ is $-j$ [using (A3) and $F=-1$ at $s=-\infty$], and then forms a diatomic product with an angular momentum given by the boundary condition at the other librational-rotational boundary. When the initial s energy is not adequate, reflection occurs and the diatomic reactant is reformed in state j .

Adiabatic invariance in each interval, plus the rotational-librational boundary conditions, has two other implications:

(1) The γ -vibrational action J_γ is larger, and hence the bending vibration is more excited, when J_γ and J_ϕ have opposite sign rather than the same sign. This result is in agreement with physical expectations, depicted in Fig. 2.³²

(2) From the boundary condition (26) imposed at the initial (i) and final (f) boundaries, and using $J_\gamma/2\pi = Fj$ [Eq. (A3)] and $F = \mp 1$ at $s = \mp \infty$, one finds

$$-j^i \pm j^f = (b^i \pm b^f)J, \quad (100)$$

where $-j^i$ and j^f denote the initial and final values of $J_\gamma/2\pi$ in this adiabatic case. (j^i and j^f are the rotational angular momenta of diatomic reactant and diatomic product, respectively.) J is the total angular momentum.

Therefore, adiabatic correlation does not necessarily imply $|j^i| = |j^f|$. In a reaction which is fairly sym-

³² The model used in Fig. 2, purely for pictorial simplicity, has (1) no interaction until a finite intermolecular distance is attained and (2) a rotational-librational boundary which is reached as soon as the molecule enters the wedge. For this model, therefore, J_γ is $-2\pi j$. J_ϕ is $2\pi(j+l)$, where l is the orbital angular momentum. Thus, for it, (26) can be rewritten as

$$4\pi |(1+b)j + bl| = J_\gamma l,$$

where b is negative ($F=-1$ initially) and $|b| < 1$. One sees that J_γ is larger when l and j have opposite signs than when they have the same sign; the resulting bending vibration is then more highly excited.

metrical in terms of mass-scaled geometry, $b^i \cong -b^f$ and the two adiabatic correlations in (100) become $j^i + j^f \cong -2b^i J$ and (if J is not too large) $j^i \cong j^f$. In a reaction, such as $\text{H} + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl}$, the final mass-scaled r_0 is small, and so $b^f \ll b^i$. In this case, the situation resembles that in Fig. 3. Now, $b^i \sim -1$, $b^f \sim 0$. When j^f in (100) is written as $J - l^f$, one finds the two correlations to be $l^f \cong j^i$ and $\frac{1}{2}(j^i + l^f) \cong J$. When $j^i \cong J$, both correlations yield $l^f \cong j^i$. That is, the final orbital and initial rotational angular momenta can be of the same order of magnitude.

NONADIABATICITY AND STATISTICAL ADIABATICITY

Changes of vibrational action J_ϕ occur when the system strikes the curved portion of Curve C with high velocity. Two terms in [(93) + (94)] for the change in J_ϕ are dependent on the initial vibration phase δ_ϕ and one is not. For any initial J_ϕ the initial distribution in δ_ϕ is uniform in the interval $(0, 2\pi)$. If averaged over the initial phase δ_ϕ the phase-dependent terms for $(J_\phi - J_\phi^0)$ vanish. Thus, J_ϕ averaged over phase δ_ϕ equals its adiabatic value, when the last term in (93) can be neglected.

The rotational-librational action J_γ changes when there is a rapidly changing torque in the rotational region, reflected in $\dot{B}$ in Eq. (69), or when there is a rapidly changing bending force constant in the librational region, reflected in $\dot{B}$ in Eq. (77). As noted earlier, when the system is near adiabatic, J_γ in the right side of (68) and (75) can be replaced by its initial value at the start of each interval. Phase averaging then makes the right hand side vanish. Thus, when it is appropriate to phase average (see below) J_γ retains its adiabatic value in each of the rotational and librational intervals.

Thereby, any initial state of the reactants yields states in the activated complex region which, when the former are phase averaged, have the same energy as the adiabatically determined states.³³ This condition

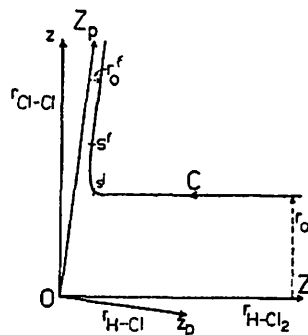


FIG. 3. Curve C in the mass-scaled xOZ subspace for $\text{H} + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl}$. Only the angle, r_0^i, r_0^f (initial and final r_0 's) are drawn to scale. Rotational-librational boundaries s^i and s^f vary with actual potential-energy surface and with energy E_γ . Oz is $r_{\text{HCl-Cl}}$.

³³ While only one J_ϕ state is formed in the adiabatic approximation, two J_γ states are formed, due to the nonadiabaticity at the rotational-librational boundary and described by (26). Thus, what we have called, for brevity, adiabatic could also be called "quasi-adiabatic," as far as the γ motion is concerned.

corresponds to the "statistical adiabaticity" mentioned in Ref. 34. A distribution of states results from the initial randomness in phase, i.e., in δ_ρ and δ_γ .

Although the initial distribution in δ_ρ and δ_γ is a uniform one experimentally, there may be a one-sided cutoff in the final distribution of J_ρ and or J_γ , or in their distribution in the activated complex region, because of the restriction of finite energy.

As noted elsewhere³⁵ statistical adiabaticity has interesting implications for activated complex theory, and we shall explore this aspect elsewhere.

STATISTICAL-DYNAMICAL THEORY OF REACTION CROSS SECTIONS

A simple approximate statistical-dynamical expression has been derived for total reaction cross sections of nearly vibrationally adiabatic reactions.³⁵ The basic concepts used in that theory receive support from an analysis of the results in the present paper, for the approximations cited. For example, the effective barrier for the s motion at the "activated complex" ($s=s^\ddagger$) was assumed to consist of the natural barrier, the usual centrifugal potential $p_\phi^2/2\mu R^2$ there, the change in adiabatic stretching vibrational energy, and, in effect (see below), a "statistical adiabatic" change of rotational to bending vibrational energy. These ideas receive support from the discussion surrounding Eq. (99). The first term is $V_1(s)$ at the barrier maximum [plus $V_2(\rho_0, s)$], the second is a contributor to ϵ_γ , the third is ϵ , and the fourth is the other contribution to a phase-averaged ϵ_γ .

Other things being equal (and sometimes they are not, for kinematical reasons), the ρ vibrational motion will be more adiabatic than the γ motion if the s kinetic energy is not too large in the regions of strong physical interaction. This result is borne out by the analysis of the previous equations: rotational or bending frequencies are lower than ρ vibrational ones, typically, and (other things being equal) have less tendency to be nonadiabatic. The above statistical-dynamical cross-section theory assumes this ρ vibrational motion to be adiabatic. The approximation would break down when the s kinetic energy is high in the region where Curve C is highly curved, as noted previously.³⁶

In the cross-section theory, the γ motion was not actually assumed to be adiabatic but rather to fulfill a "quasiequilibrium" condition which is closely related to the statistical adiabaticity of the γ motion considered in the previous section.

The present solutions indicate how, with extension to three dimensions, the cited theory for total reaction cross sections could be extended to one for differential cross sections, but this extension is deferred until a later publication.

³⁴ R. A. Marcus, Discussions Faraday Soc. 44, 7 (1967).

³⁵ R. A. Marcus, J. Chem. Phys. 45, 2630 (1966); 46, 959 (1967).

RELATED APPLICATIONS

A "vibrationally adiabatic" reactive collision is a chemical analog of the elastic collision in physical scattering.³⁴ In both physical and reactive scattering, however, when too extensive an excitation or de-excitation of the internal degrees of freedom occurs the cited approximation may cease to be a useful starting point in a successive approximation scheme.

With this preamble several applications may be noted. Some provide insight into assumptions made in various statistical models such as the activated complex theory of rate constants, the statistical-dynamical theory of reaction cross sections mentioned in the previous section, and a phase space theory of reactions³⁶ (conditions of validity and limitations of which we hope to discuss in a later paper).

Again, the comparison of the exact computer results with the equations derived earlier is of interest in that it provides some idea of the range of applicability of the assumptions: near adiabaticity, zeroth-order neglect of γ , ρ interactions. (Some idea of this range is also obtained by perturbation theory.) In turn, within this range these theoretical expressions help provide insight into the various computer results and permit a prediction of how various changes in the potential energy surface should effect the computer results.

We note that a distribution in final J_i 's occurs as a result of the random distribution in initial phases, for any given initial values of these action variables and of the initial kinetic energy $\mu s^2/2$ of relative translational motion. For comparison with the present theory it would be useful to present the exact computer results in a way which permits a comparison of these final J_i distributions, at fixed initial J_i 's and $\mu s^2/2$, and which permits a comparison with results which have been averaged over initial orbital angular momentum in the usual kinetic manner. The comparison may be made for those potential energy surfaces for which the principal configurations of the ABC system at small s are near linear. When they are nonlinear, it was noted in Part III that the treatment given there, and hence here also, is modified.

The present expressions suggest how to compare the computer results for one and two dimensions. The latter contains an adiabatic energy $\epsilon_\gamma(s)$ of the γ , ϕ motions, which adds to the effective potential for the s motion. In the comparison, some allowance for this difference can be made.

APPENDIX I. MOMENTS OF INERTIA, ORIENTATIONS, AND ANGULAR MOMENTA IN NATURAL COLLISION COORDINATES

All distances are mass scaled, as in Glossary.

³⁶ J. C. Keck, J. Chem. Phys. 29, 410 (1958); P. Pechukas and J. C. Light, *ibid.* 42, 3281 (1965).

Distances, Orientations, and Moments of Inertia

In Appendix I of Part III it was shown that at large $\pm s$ the internuclear distance of the diatomic species is r , and in the case of reaction in a spaced-fixed ($^0x_a0^0y_a$) plane the angle between the 0x_a axis and the axis of the diatomic species is $\phi + f\gamma$, where $f = -1$ at large $-s$ and $+1$ at large $+s$. The internuclear axis is drawn from A to B (large $-s$) or B to C (large $+s$) in Reaction (1). (See Part III, Appendix II.) At large $|s|$, incidentally, $f = F$, so the above angle can be written as $\phi + F\gamma$.

Similarly, it was shown that the line of centers of the two species made an angle ϕ with the 0x_a axis at large $\pm s$ and had a length Z (large $-s$) or Z_p (large $+s$). One finds from the definition of R in Part III and Eqs. (A1) and (A2) of Appendix I there that the separation distance of the two species at large $\pm s$ is $(R^2 - r^2)^{1/2}$. [This line of centers is drawn from AB to C (large $-s$) or A to BC (large $+s$).]

Thus, at large $\pm s$ the moment of inertia of the diatomic species and the "orbital" moment of inertia of the two reactants (large $-s$) or products (large $+s$) are μr^2 and $\mu(R^2 - r^2)$, respectively. When the diatomic species at large $\pm s$ has its equilibrium bond length, one finds in Part III that $r = r_0$ and $R = R_0$, so that the two moments are μr_0^2 and $\mu(R_0^2 - r_0^2)$ then.

At small s , one finds from Part III, the moment of inertia of the near-linear ABC system is μR^2 and the internuclear axis makes an angle of ϕ with the (space-fixed) 0x_a axis for reaction in a plane. When this ABC is in its most stable configuration (stable with respect to bending and symmetric stretching only) μR^2 becomes μR_0^2 .

Angular Momenta

Since $F^2 = 1$ at large $\pm s$ the last terms in (2) can be written as a sum of squares

$$\frac{1}{2}\mu r^2(\phi + F\gamma)^2 + \frac{1}{2}\mu(R^2 - r^2)\phi^2.$$

These two terms constitute the rotational energy of the diatomic species and the orbital kinetic energy of the two reactants (or products), respectively, since $\phi + F\gamma$ and ϕ are the respective coordinates and μr^2 and $\mu(R^2 - r^2)$ are the respective moments of inertia. Thus, the rotational and orbital angular momenta, j and l , respectively, are $\partial T / \partial(\phi + F\gamma)$ at constant ϕ and $\partial T / \partial\phi$ at constant $\phi + F\gamma$. Thereby,

$$j = \mu r^2(\phi + F\gamma), \quad (A1)$$

$$l = \mu(R^2 - r^2)\phi. \quad (A2)$$

The total angular momentum J is $j + l$.

At large $\pm s$, Eqs. (2), (A1), and (A2) also show that

$$\begin{aligned} p_\phi &= \mu R^2 \dot{\phi} + \mu r^2 F \dot{\gamma} = J, \\ p_\gamma &= \mu r^2 \dot{\gamma} + \mu r^2 F \dot{\phi} = jF. \end{aligned} \quad (A3)$$

Thus, we have

$$l = J - j = p_\phi - F p_\gamma = (J_\phi - F J_\gamma) / 2\pi \quad (A4)$$

since $J_\phi = 2\pi p_\phi$ and $J_\gamma = 2\pi p_\gamma$ at large $|s|$.

APPENDIX II. MODIFICATIONS FOR A TWO-REACTION PATH SYSTEM

In some reactions both BC and AB may form. Then, in addition to Curve C there is a second curve to be considered, leading to a product AC instead of BC. This curve, denoted by G in Part III, is obtained from C by reflection about the OZ axis in the zOZ plane in Fig. 1.

Since the natural collision coordinates n and s are defined with respect to Curve C, corresponding coordinates should be defined with respect to Curve G, as noted in III. Any point can be defined with respect to one coordinate set or the other, but in the curved region of Curve C it is useful to define by n, s only the position of those points close to C. Similar remarks apply to G.

Thus, when a system in the curved region can easily move from the C neighborhood to the G one (i.e., if there is a small γ barrier at that s) it is better to replace the coordinates defined with respect to C and those defined with respect to G by another set which treats C and G symmetrically. This definition is not attempted in the present paper. Instead, we confine our attention to systems in which the γ barrier becomes high (i.e., $k > 1$) before Curve C becomes appreciably curved. Since the coordinates r and γ are actually defined symmetrically with respect to Curves C and G where C is not curved (they are cylindrical coordinates in this region, the OZ axis being the axis of the cylinder, r the distance from OZ and γ the angle about OZ), the coordinates satisfy the desired symmetry condition. After the system enters the ($k > 1$) region and the Curve C (and G) becomes curved, only the coordinates defined with respect to C need be used in considering the formation of products A and BC and the lack of symmetry of coordinates in that region is irrelevant. Similar remarks apply to Curve G and to the formation of products AC and B.

Instead of (43) the γ potential function for the present case, with coordinates defined with respect to Curve C, say, is

$$V_2(0, \gamma, s) = \frac{1}{2}(1 - \cos 2\gamma)A(s). \quad (A5)$$

The resulting modifications are as follows:

- (1) In Eq. (45) $\gamma/2$ is replaced by γ .
- (2) *Case (ai)*. Equations (50) and (52) are unchanged. The right side of (51) becomes $F(\gamma, k)/4K(k)$ and a similar change occurs in (53).
- (3) *Case (aii)*. In Eq. (55) $\gamma_0/2$ is replaced by γ_0 . The right sides of (61) and (63) are multiplied by $\frac{1}{2}$ and 2, respectively. Equation (62) is unchanged but now $\sin\beta$ is $k \sin\gamma$ instead of $k \sin\frac{1}{2}\gamma$. Equation (64) is unchanged. (The corrections to the other equations are evident from these corrections.)
- (4) *Case (bi)*. In (65) and (66) the $\sin^2\gamma/2$ is replaced by $\sin^2\gamma$. Equations (68) and (69) are unchanged but u is now $4Kw_\gamma$. In Eq. (70) $\cos 2\pi w_\gamma$ is replaced by $\cos 4\pi w_\gamma$.
- (5) *Case (bii)*. The right sides of (74)–(77) should be multiplied by a factor of $\frac{1}{2}$. In (74) γ_0 is replaced by $\gamma_0/2$, and u_0 is $4w_\gamma F(\gamma_0, k)$. In (75) u_1 is $4w_\gamma K_1$, as before.

The two-reaction path system has a rotational-librational boundary condition which differs somewhat from (26). The integral $\oint p_\gamma d\gamma$ on the rotational side of the boundary is again given by (25). On the libra-

tional side, the contribution of the first term on the right side of (23) again vanishes over the librational cycle, and the limits in (24) are $a_1=0$, $a_2=\pi$, for the given reaction path. We thus have

$$J_\gamma^l = 2 \int_0^\pi [2I(E_\gamma - V_2^0)]^{1/2} d\gamma, \quad (\text{A6})$$

$$\begin{aligned} J_\gamma^r &= bJ_\phi \pm \int_0^{2\pi} [2I(E_\gamma - V_2^0)]^{1/2} d\gamma \\ &= bJ_\phi \pm 2 \int_0^\pi [2I(E_\gamma - V_2^0)]^{1/2} d\gamma. \end{aligned} \quad (\text{A7})$$

Elimination of the integral yields

$$J_\gamma^l = |J_\gamma^r - bJ_\phi| \quad (\text{A8})$$

instead of (26).

Similarly, if the system ends up on the other reaction path the latter obeys a boundary condition given by (A8).