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A Generalization of the Activated Complex Theory of Reaction Rates

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Abstract

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In its usual form activated complex theory assumes a quasi-equilibrium between reactants and activated complex, a separable reaction coordinate, a Cartesian reaction coordinate, and an absence of interaction of rotation with internal motion in the complex. In the present paper a rate expression is derived without introducing the Cartesian assumption. The expression bears a formal resemblance to the usual one and reduces to it when the added assumptions of the latter are introduced. The new equation for the transmission coefficient contains internal centrifugal terms. The derivation employs an extension of the Stackel-Robertson formalism for separation of variables in mechanics. The fourth assumption can also be weakened and a rotational interaction included in the formalism. In applications of the rate equation use is made of the recent finding that in the immediate vicinity of a saddle-point or a minimum a potential energy surface can be imitated in some major topographical respects by a surface permitting separation of variables. The separated wave equation for the reaction coordinate is then curvilinear because of the usual curvature of the path of steepest ascent to the saddle-point. Calculations of transmission coefficients and rates can be made and compared with those obtainable from the usual one-dimensional Cartesian-like calculations on the one hand and with some based on the numerical integration of the n-dimensional Schrodinger equation on the other. An application to a common three-center

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problem is discussed.

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Introduction

In activated complex theory the reaction coordinate has been assumed to be Cartesian and, in quantum mechanical treatments at least, to be dynamically separable from the other coordinates.^{1,2} The effect of any rotational constants of the motion on the internal motion of the activated complex has normally been neglected,³ and equilibrium between reactants and activated complexes has been assumed.⁴

In the present paper and in a companion one⁵ on the classical mechanical formulation, this activated complex theory is generalized by extending it to curvilinear reaction coordinates and, within certain limitations,⁶ by including the effect of the constants of the motion on the internal motion of the activated complex. The assumption of separability will be made in the quantum formulation. It now has^{somewhat} wider applicability than before because of the availability of a recent local approximation method for nonseparable surfaces.⁷ Separability will not be assumed in the classical mechanical formulation, however.⁵

The desirability of extending activated complex theory to include curvilinear reaction coordinates is clear from an examination of the local topography of the potential energy surface near the saddle-point, when that saddle-point occurs: The path of steepest ascent to this point, the "reaction path", is almost invariably a curve in mass-weighted configuration space, rather than a straight line. In some major topographical respects this surface can be matched locally by one permitting separation of variables.⁷ The reaction coordinate is then found to be curvilinear. This coordinate is this approximately separable one near the saddle-point, a coordinate which leads from the "reactants' region" of mass-weighted configuration space to the products' region in that neighborhood.

Except in computer calculations⁸ or in early discussions based on the motion of balls on surfaces,⁹ the dynamical effects of the curvature of the reaction path

have been ignored in the literature. The curvilinear character gives rise dynamically to a centrifugal effect, an effect smaller at the saddle-point than at a short distance from it, where the kinetic energy is greater. As discussed in detail elsewhere⁷ the net result is to make the reaction coordinate in mass-weighted configuration space have a smaller curvature than the reaction path. The centrifugal effect introduces a coupling between the reaction coordinate and the vibrations of the complex, just as the rotation of a molecule as a whole can influence the latter's vibration by a centrifugal potential. The^{above} effect occurs in classical mechanics and, phrased in terms of probabilities, in quantum mechanics when the system has enough energy to surmount the barrier. At low energies nuclear tunneling occurs and, the formulae suggest, so does a non-classical centrifugal effect, negative in nature.

We consider first the case where the dependence of the properties of the activated complex on the rotational constants of the motion can be neglected. In a later section the effect of the rotational state on the behavior of the activated complex is considered.

The basic equation, Equation (21) below, reduces to the

usual activated complex expression when the reaction coordinate is treated as a Cartesian one. Equation (21) may be used to consider several nonseparable n-dimensional problems by introducing into it the local approximation method mentioned earlier.¹⁰ Comparison with computer calculations will then permit an assessment of the useful range of that local approximation and should also facilitate the physical interpretation of such calculations.

Schrödinger Equation and Separated Equations

Certain curvilinear coordinate systems will serve as better starting points for finding separable approximations to the non-separable potential energy function. We shall suppose that a coordinate in one of these has been selected as the reaction coordinate; the process of making the selection has been briefly discussed elsewhere.⁷ For example, in the case of a three-center atom transfer reaction involving a linear activated complex ($A + BC \rightarrow AB + C$) the reaction path in mass-weighted configuration space leading from reactants to products is a curved one. For such paths in the vicinity of the saddle-point region, circular cylinder, parabolic cylinder, or elliptic cylinder coordinates are much more appropriate than the usual Cartesian ones. Should both the vibrational path of steepest ascent from the critical point and the reaction path both be curved in this space, and should one wish to include this feature, only parabolic or elliptic cylinder coordinates would be appropriate.⁷

In curvilinear coordinates q^1, \dots, q^n the Schrödinger equation has the form (1).¹¹

$$H\Psi = \alpha_1 \Psi, \quad (1)$$

where H is the Hamiltonian operator, α_1 the total energy, and Ψ the wave function of the entire system.

$$H = \frac{-\hbar^2}{2} \sum_{s,t=1}^n \frac{1}{g^{\frac{1}{2}}} \frac{\partial}{\partial q^s} g^{\frac{1}{2}} g^{st} \frac{\partial}{\partial q^t} + U \quad (2)$$

The q^s are generalized coordinates, and U is the potential energy; g^{st} is a contravariant tensor¹² conjugate to the metric tensor g_{st} appearing in the line element ds in mass-weighted space; g is the determinant of the g_{st} .

$$g^{st} = \sum_{i=1}^n \frac{1}{m^i} \frac{\partial q^s}{\partial x^i} \frac{\partial q^t}{\partial x^i}; \quad g_{st} = \sum_{i=1}^n m^i \frac{\partial x^i}{\partial q^s} \frac{\partial x^i}{\partial q^t} \quad (3)$$

$$ds^2 = \sum_{s,t=1}^n g_{st} dq^s dq^t; \quad \sum_{r=1}^n g_{sr} g^{rt} = \delta_s^t \quad (4)$$

where x^i is a Cartesian coordinate of an atom of mass m^i ; the coordinates of the k 'th atom are given by $i = 3k, 3k + 1, 3k + 2$. Both g_{st} and g^{st} are symmetric tensors.

Under certain conditions on U and on g^{st} , Eq. (1) can be separated into m individual equations, each depending on its own set of variables.¹³ The wave function Ψ then becomes (5).

$$\Psi = \prod_{\mu=1}^m \Psi_{\mu} \quad (5)$$

where Ψ_{μ} is the wave function for the μ 'th set. As a particular case of this separation one could select one set of variables to consist of a single variable, the reaction coordinate, q^r , and select a second set to consist of all remaining coordinates. I.e., $m = 2$ then. Under the assumed conditions¹³ g^{st} vanishes when s and t belong to different sets.

As a result of the separation the Hamiltonian operator has the form (6).¹³

$$H = \sum_{\mu=1}^m (\phi^{\mu 1} / f_{\mu}) H_{\mu} + U \quad (6)$$

where H_{μ} is a Hermitian differential operator (7). The potential energy U is of the form (8), and $\phi^{\mu 1}$ and f_{μ} are defined below.

$$H_{\mu} = \frac{-\hbar^2}{2} \sum_{i,j=1}^{h_{\mu}} \frac{\partial}{\partial q^{\mu_i}} f^{\mu_i \mu_j} \frac{\partial}{\partial q^{\mu_j}} \quad (7)$$

$$U = \sum_{\mu=1}^m \phi^{\mu 1} X_{\mu} \quad (8)$$

The separated equations are:

$$(H_{\mu} + X_{\mu} f_{\mu}) \psi_{\mu} = \sum_{\nu=1}^m \alpha_{\nu} \phi_{\mu\nu} f_{\mu} \psi_{\mu} \quad (9)$$

q^{μ_i} is the i 'th coordinate in set μ (there are h_{μ} such coordinates), and f_{μ} is the h_{μ} 'th root of the $h_{\mu} \times h_{\mu}$ determinant of the $f^{\mu_i \mu_j}$. The quantities $\phi_{\mu\nu}$ and $f^{\mu_i \mu_j}$ depend only on the properties of the metric. They are functions of the coordinates in the μ 'th set only and are independent of the potential energy function; X_{μ} also depends only on the coordinates of set μ . The $\phi_{\mu\nu}$ are conjugate to the $\phi^{\mu\nu}$ and may be called the Stäckel coefficients.¹⁴

$$\sum_{\mu=1}^m \phi^{\mu\nu} \phi_{\mu\lambda} = \delta_{\lambda}^{\nu} \quad (10)$$

The $\phi^{\mu 1}$ are given by (11) and the $f^{\mu_i \mu_j}$ by (12).

$$\phi^{\mu 1} = (\det g^{\mu_i \mu_j})^{1/h_{\mu}} \quad (11)$$

where i and $j = 1$ to h_{μ} .

$$f^{\mu_i \mu_j} = g^{\mu_i \mu_j} f_{\mu} / (\det_{i,j=1}^{h_{\mu}} g^{\mu_i \mu_j})^{1/h_{\mu}} \quad (12)$$

The determinant of the $\phi_{\mu\nu}$, Φ , is related to g and to the f_{μ} :

$$g^{\frac{1}{2}} = \Phi \prod_{\mu=1}^m f_{\mu} \quad (13)$$

Various coordinate systems for which separation of variables can be made have been described by Eisenhart^{15,16} for the case where $h_{\mu} = 1$ for all μ . He has given the corresponding $\phi_{\mu\nu}$'s and f_{μ} 's and his results can be at least partly adapted to the present case where h_{μ} need not be unity. Typical approximations in the literature of molecular dynamics correspond, incidentally, to setting many of the $\phi_{\mu\nu}$'s equal to zero and many of the g^{rs} equal to zero or to constants.

The Local Approximation

As mentioned earlier it will be supposed that it has been possible to describe a coordinate system such that one of the coordinates is dynamically separable from all remaining coordinates in the activated complex region and tends to lead in this vicinity from the reactants' "region" to the products' one. This coordinate is then the "reaction coordinate". When the potential energy function has a saddle-point the choice of this separable coordinate could be made as described elsewhere.⁷ (The potential energy surface is approximated by one which permits separation of variables.¹⁷) The reaction coordinate forms one of the sets μ mentioned earlier. It will be described by setting μ equal to r . Since only the nonseparable potential energy surface in the vicinity of the saddle-point region is being approximated by a separable surface, the properties in the separated system for the degrees of freedom other than q^F are those of the activated complex rather than of the reactants.

Parenthetically, it may be noted that this matching of the two energy surfaces will normally be poorer for configurations far from the activated complex region. However, when most of the scattering of the incident wave along the reaction coordinate occurs near the activated complex region, this poor fit for configurations remote from those of the complex will only be of minor concern.

Since the wavelength (more precisely, the reciprocal of the component

of the wave vector along q^r) is large in the activated complex region **because of the low kinetic energy there**, and since the potential energy changes rapidly there, most of the scattering may in fact occur in that region. Indeed, the phase integral expression ¹⁸ for tunneling points up this local scattering characteristic.

The coordinate curves for separable systems are of two types, open and closed, the former extending to infinity. Examples of the closed type are circles and ellipses. Such a curve would provide a convenient coordinate only if most of the scattering occurred over a relatively small portion of the arc. Then, the error of replacing an ^{actual} open path by an arc of a closed one becomes minor. We consider an example later.

Probability Distribution

Near any point sufficiently far from the saddle-point region, along the reaction coordinate q^r in the separable potential energy surface, the potential energy varies relatively little with distance and the component of the momentum along this coordinate is real and relatively large. Classical statistics may then be used for q^r there but not necessarily for the other coordinates. The wave function of all degrees of freedom but q^r will be denoted by ψ' :

$$\psi' = \prod_{\mu \neq r} \psi_{\mu}(q^{\mu_1}, \dots, q^{\mu_n_{\mu}}) \quad (14)$$

For any given value of q^r and of the conjugate momentum p_r the state of the remaining degrees of freedom can be **regarded as describable** by a (discrete) quantum number λ : In the case of ^{an} isolated gaseous activated complex molecule confined in a volume, even the translational state can be regarded as quantized. In the case of any activated complex in solution, a macroscopic subsystem can be regarded as the complex. It can be placed in a box and the $n-1$ degrees of freedom regarded as given rise to discrete eigenvalues, characterized by the quantum number λ , **for purposes of the present discussion.**

Inspection of the separated equations (9) and (A4) (Appendix I) shows that ψ' depends on the separation constants a_1, \dots, a_m . For any given value of q^r these constants determine λ and p_r , and conversely. Unlike p_r and q^r **the** a 's are constants of the motion, however.

The probability of the system being in a quantum state described by λ and of being in any small element $\Delta q^r \Delta p_r$ will be denoted by $P(\lambda, q^r, p_r, T) \Delta q^r \Delta p_r$. We shall suppose that the reactants are in statistical equilibrium with this system. Since the probabilities of the system being in $\Delta q^r \Delta p_r$ and of having any given value of λ are independent and since the number of quantum states in $\Delta q^r \Delta p_r$ is $\Delta q^r \Delta p_r / h$, one obtains:

$$P(\lambda, p_r, q^r, T) = e^{-\alpha_1(\lambda, p_r)/kT} / h Q_1 \quad (15)$$

where the given values of p_r , q^r and λ automatically fix the total energy α_1 and where $\exp(-\alpha_1/kT)$ is the Boltzmann factor. Q_1 is the partition function of the reactants.

In any one of these quantum states we may take Δq^r so small that none of the quantities $\phi_{\mu\nu}$, g^{ij} or g vary over it.

When a system is in any one of these quantum states its probability of being in any volume element $g^{\frac{1}{2}} \prod_{i=1}^n dq^i$ can be written as $|\psi|^2 A(q^r) g^{\frac{1}{2}} \prod_{i=1}^n dq^i$, where $A(q^r)$ is a normalizing factor for this state.

In this classical approximation for the q^r coordinate,

$A(q^r)$ can be treated as a constant over Δq^r . Integration over all q^i shows that $A(q^r)$ equals $1/\Delta q^r \int |\psi|^2 g^{\frac{1}{2}} \prod_{i \neq r} dq^i$.

Thus, the probability of find the system in the range $dp_r \prod_{i=1}^n dq^i$ and in the state λ is $P_{(p)}(\lambda, p_r, q) dp_r \prod_{i=1}^n dq^i$, where

$$P_{(p)}(\lambda, p_r, q) = \frac{e^{-\alpha_1(\lambda, p_r)/kT} |\psi|^2 g^{\frac{1}{2}}}{h Q_1 \int |\psi|^2 g^{\frac{1}{2}} \prod_{i \neq r} dq^i} \quad (16)$$

and q denotes the totality of coordinates (q^1, \dots, q^n) .

For each (discrete) value of λ , any of the α_k depends continuously on p_r , except as noted below. The probability of finding the system in $d\alpha_k \prod_{i=1}^n dq^i$ and in the state λ is obtained by replacing dp_r above by $(\partial p_r / \partial \alpha_k)_\lambda d\alpha_k$. Upon denoting this probability by $P(\alpha_k, \lambda, q) d\alpha_k \prod_{i=1}^n dq^i$ and evaluating $(\partial p_r / \partial \alpha_k)_\lambda$ in Appendix I we find

$$P(\alpha_k, \lambda, q) = \frac{e^{-\alpha_k/kT} |\psi'|^2 g^{\frac{1}{2}}}{h Q_1 p_r \int |\psi'|^2 \phi^{rk} g^{\frac{1}{2}} \prod_{i \neq r} dq^i} \quad (17)$$

With the aid of (17) it will be possible to express the reaction rate in a form involving summation and integration over the constants of the motion. This step was not possible from (15) or (16).

The above transformation from the (p_r, λ) space to the (α_k, λ) space is permissible only for those α_k 's for which the denominator does not vanish, i.e. for which $\phi^{rk} \neq 0$. The vanishing of ϕ^{rk} implies, as one can see from Eq. (A10) of Appendix I, that α_k does not depend on p_r when λ is held constant. An example is cited later.

It will be convenient to introduce the notation:

$$(\psi', \psi')_{rk} = \int |\psi'|^2 \frac{\phi^{rk}}{f_r} g^{\frac{1}{2}} \prod_{i \neq r} dq^i \quad (18)$$

From Eq. (13) one has:

$$\phi^{rk} g^{\frac{1}{2}} / f_r = \phi^{rk} \prod_{\mu \neq r} f_\mu \quad (19)$$

Since ϕ^{rk} is the cofactor of ϕ_{rk} in the determinant ϕ (cf Eq. 10), it does not contain the r 'th row $\phi_{r\mu}$ and so does not depend on q^r ; neither does $\prod_{\mu \neq r} f_\mu$ and, so, neither does $(\psi', \psi')_{rk}$. If the wave function in the n -dimensional system were normalized so that $(\psi', \psi')_{r1}$ equalled unity, the wave function would be normalized to unit incident probability current.

Calculation of the Reaction Rate

Total and potential energies will be measured relative to the potential energy of the most stable configuration of the activated complex. Q_1 then denotes the partition function of the reactants measured relative to this energy zero. We let Q denote the usual partition function of the reactants, i.e., measured relative to the potential energy of their most stable configuration. If ΔU is the potential energy of the most stable configuration of the activated complex minus that of the most stable one of the reactants then Q_1 equals $Q \exp(\Delta U/kT)$.

To obtain k_{rate} from (17), one notes that (17) is to be multiplied by the velocity \dot{q}^r , by $\prod_{i \neq r} dq^i$ and by the transmission coefficient $\kappa(\alpha_k, \lambda)$, ^{then} summed over all λ and integrated over all values of α_k and over all q^i ($i \neq r$). Upon observing that \dot{q}^r equals $\delta^{r1} p_r$ the final expression for k_{rate} is found to be:

$$k_{\text{rate}} = \frac{kT}{h} \frac{e^{-\Delta U/kT}}{Q} \int_{\alpha_k} \sum_{\lambda} \kappa(\alpha_k, \lambda) e^{-\alpha_1/kT} \frac{(\psi', \psi')_{r1}}{(\psi', \psi')_{rk}} d\alpha_k/kT \quad (20)$$

(k = 1, \dots, m)

where α_1 is a function of α_k and λ .

For any preassigned value of α_k , the remaining α 's take on discrete values, reflected by the quantum numbers λ . Accordingly, Eq. (20) can be rewritten in a slightly more symmetrical form:

$$k_{\text{rate}} = \frac{kT}{h} \frac{e^{-\Delta U/kT}}{Q} \int_{\alpha_k} \sum_{\substack{\alpha_j \\ j \neq k}} \kappa(\alpha) e^{-\alpha_1/kT} \frac{(\psi', \psi')_{r1}}{(\psi', \psi')_{rk}} d\alpha_k/kT \quad (21)$$

where α denotes totality of α 's, $(\alpha_1, \dots, \alpha_m)$ and where each ψ_μ is a function of $(q^{\mu_1}, \dots, q^{\mu_h}, \alpha_1, \dots, \alpha_m)$.

When α_k is taken to be α_1 , one finds:

$$k_{\text{rate}} = \frac{kT}{h} \frac{e^{-\Delta U/kT}}{Q} \int_{\alpha_1} \sum_{\substack{\alpha_j \\ j \neq 1}} \kappa(\alpha) e^{-\alpha_1/kT} d\alpha_1/kT \quad (22)$$

The lower limit on α_1 is $-\Delta U$, though in practice the exact value of the lower limit hardly affects k_{rate} , since most of the contribution to the integral comes from values of α_1 near the top of the barrier, i.e., values near zero.

In calculations of the rate constant itself, Eq. (22) appears to be the most useful form of (21), at least when most of the activated complexes are formed in low vibrational states for coordinates interacting with the reaction coordinate: Its

use avoids the calculation of $(\psi', \psi')_{r1}$ and $(\psi', \psi')_{rk}$ and also permits a direct comparison to be made of the values of $\kappa \exp(-a_1/kT)$ for the curvilinear and for the usual Cartesian approximation. The comparison can be made as a function of a_1 for each vibrational state of the activated complex. On the other hand, for an examination of the manner in which the curvilinear formula for k_{rate} approaches the Cartesian one, Eq. (21) with some \underline{k} other than $\underline{1}$ is useful, as shown in some examples described later.

Transmission Coefficient

The transmission coefficient $\kappa(\alpha)$ is the ratio of transmitted to incident probability currents for the given value of the constants of the motion, α . To calculate κ an expression for the probability current in curvilinear coordinates must be used. This expression has been given elsewhere in terms of the wave function along this coordinate.¹³ The phase integral method can be used for a semi-classical estimate of κ , incidentally, since the Schrödinger-type equation for the reaction coordinate (Eq. 9 with $\mu = r$) can readily be adapted to this calculation. An improved formula for the semi-classical estimate, one which takes cognizance of the proximity of the two transition points for the case of energies below the top of the barrier, is available and will be discussed elsewhere.²⁰

An Application of Eq. (21)

By way of example, we consider a three-center problem, $A + BC \longrightarrow AB + C$, proceeding via a linear collision-complex. In mass-weighted configuration space the reaction path is curved.^{9,21} As mentioned earlier, this path can be matched in the local approximation by the corresponding path for a surface which permits separation of variables. The matching has been discussed previously⁷ and, in the following discussion, will be regarded as having been performed.

The plane defined in mass-weighted configuration space by the tangent and principal normal to the reaction path, the osculating plane of this path, will be called the "plane of reaction". In many diagrams^{9,21} in the literature one assumes for simplicity that the reaction coordinate lies in a plane determined only by the AB and BC interatomic distances, mass-weighted as in Eq. (3). The remaining degrees of freedom are taken to be dynamically uncoupled from these two in those discussions. We consider this special case first.

In terms of the properties of a suitable coordinate system for matching of the potential energy functions, the latter assumption leads to a choice of a cylindrical coordinate system (Cartesian, circular, parabolic or elliptic cylinder):⁷ The Z-axis, which is normal to the plane of reaction, represents the set of all degrees of freedom but the AB and BC distances. The latter two coordinates can be used to describe any point in the plane. In Eq. (6) one has then three sets, $m = 3$. With proper choice of coordinates one can diagonalize the kinetic energy contribution of the co-

ordinates in the plane of reaction and normalize their coefficients such that for two Cartesian coordinates in this plane the g^{ss} are unity. One can choose a scaling factor for the remaining coordinates (represented metrically by the Z-axis) so that the $\det g^{\mu_i \mu_j}$ is unity.

When the reaction coordinate is arbitrarily assumed to be a straight line, as in the usual treatment in the literature, it suffices to consider only two sets of coordinates, as in Example 1 below,

instead of three sets. It is shown there that this neglect of reaction coordinate curvature permits one to obtain the standard literature rate expression from Eq. (21). The effect of curvature is then discussed in Example 2 using a circular cylinder metric and in Examples 3 and 4, more briefly, using elliptic cylinder and parabolic cylinder metrics. When the reaction is symmetrical, e.g., when $A + BA \rightarrow AB + A$, the vibration of the activated complex in the plane of reaction is rectilinear and Examples 2 and 3 apply. However, when the vibrational coordinate curve in the plane of reaction is not a straight line, and when one wishes to describe this curvature, one of the coordinate systems in Examples 3 or 4 should be used. The various $\phi_{\mu\nu}$'s, f_{μ} 's, and g^{st} 's are known for a variety of coordinate systems.^{15,16}

The above cylinder coordinate systems can also be used to represent a more general picture of the three-center reaction in which additional coordinates besides the two bond distances are permitted to contribute to the plane of reaction. If one considers the n-dimensional curve describing the reaction path in mass-weighted configuration space, the osculating plane of the path would be taken to be the plane normal to the Z-axis. One then proceeds as before.

Some applications of Eq. (22) to the calculation of the rate constant using some of the following coordinate systems and reaction coordinates will be reported elsewhere.¹⁰ The present discussion will be concerned instead with an amplification of the preceding discussion, with showing in Example 1 how the usual activated complex theory equation in the literature is a special case of Eq. (21), and with discussing in Examples 2 and 3 the approach of the curvilinear formulae embodied in (21) to the Cartesian one. A suitable choice of k for the latter purpose will be described.

Example 1. Cartesian Metric.

With m equal to 2 the $\phi_{\mu\nu}$'s for the Cartesian metric are given by (23).¹⁶

$$\begin{pmatrix} \phi_{11} & \phi_{12} \\ \phi_{21} & \phi_{22} \end{pmatrix} = \begin{pmatrix} 1 & -1 \\ 0 & 1 \end{pmatrix} \quad (23)$$

One must first determine which ϕ^{rk} 's in Eq. (21) vanish. Since ϕ^{1j} is the co-factor of ϕ_{1j} in ϕ , it is seen from (23) that only ϕ^{12}

is zero. Thus, if q^1 is selected as the reaction coordinate, the continuous variable α_k in Eq. (21) should not be taken to be α_2 . Otherwise, it makes no difference whether q^1 or q^2 is selected. We choose q^2 to be q^r and α_k to be α_2 . The Ψ_2 -equation for the reaction coordinate then depends only on α_2 , so κ depends only on α_2 . The Ψ_1 -equation for the other degrees of freedom depends only on $(\alpha_1 - \alpha_2)$, which thereby takes on discrete values. They are denoted below by α_1' . Since α_1 equals $(\alpha_1 - \alpha_2) + \alpha_2$, Eq. (21) then reduces to (24):

$$k_{\text{rate}} = \frac{kT}{h} \frac{Q^\ddagger}{Q} e^{-\Delta U/kT} \int \kappa(\alpha_2) e^{-\alpha_2/kT} d\alpha_2/kT \quad (24)$$

where Q^\ddagger is the partition function of the activated complex, $\sum_{\alpha_1'} \exp(-\alpha_1'/kT)$. When tunneling is neglected, $\kappa(\alpha_2)$ vanishes for $\alpha_2 < 0$. In the same classical approximation it is unity for $\alpha_2 \geq 0$, as one sees at once from the Ψ_2 equation.

¶ Eq. (24) is equivalent to the standard equation in the literature for the activated complex theory.^{1,21}

Example 2. Circular Cylindrical Coordinates.

We take $q^1 = r$ and $q^2 = \cos \theta$ when r and θ are the usual polar coordinates. The $\phi_{\mu\nu}$'s are given by:¹⁶

$$\begin{pmatrix} \phi_{11} & \phi_{12} & \phi_{13} \\ \phi_{21} & \phi_{22} & \phi_{23} \\ \phi_{31} & \phi_{32} & \phi_{33} \end{pmatrix} = \begin{pmatrix} 1 & (-1/q^1)^2 & -1 \\ 0 & 1/(1-q^2)^2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (25)$$

The reaction coordinate is taken to be along the arc of a circle and, therefore, to be q^2 . Use

of this coordinate system implies that the potential energy surface, plotted in mass-weighted coordinates, is symmetrical along q^1 about the saddle-point region.

From (25) ϕ_{11}^{21} , ϕ_{11}^{22} and ϕ_{11}^{23} are found to be $1/q^1$, 1 and 0, respectively. Hence, α_1 , or α_2 but not α_3 may be picked as α_k to avoid a singular transformation.

To show the approach of Eq. (21) to a Cartesian formula in this case we shall

select α_2 , since the Ψ_2 -equation (and hence \mathcal{K}) depends only on α_2 . The Ψ_3 -equation depends only on α_3 , which takes on discrete values. The Ψ_1 -equation depends on $\alpha_1 - \alpha_3 = \alpha_2/(q^1)^2$. For any preassigned value of α_2 , $\alpha_1 - \alpha_3$ then takes on discrete values.

Let $\alpha' = \alpha_1 - \alpha_3$. Noting that $\alpha_1 = \alpha_3 + \alpha'$, Eq. (21)

becomes

$$k_{\text{rate}} = \frac{kT}{h} e^{-\Delta U/kT} \frac{Q_3^\ddagger}{Q_0} \int_{\alpha_2} \kappa(\alpha_2) \left[\sum_{\alpha'} e^{-\alpha'/kT} \left\langle \frac{1}{q_1^2} \right\rangle_{\alpha', \alpha_2} \right] d\alpha_2/kT \quad (26)$$

where Q_3^\ddagger denotes $\sum_{\alpha_3} \exp(-\alpha_3/kT)$, the partition function for all coordinates of the activated complex other than q^1 and q^2 , and where $\langle \rangle$ denotes an average value:

$$\langle L \rangle = \int |\psi'|^2 L \prod_{\mu \neq r} f_\mu \prod_{i \neq r} dq^i / \int |\psi'|^2 \prod_{\mu \neq r} f_\mu \prod_{i \neq r} dq^i \quad (27)$$

The average depends on the subscripts indicated in (26), α' and α_2 , because ψ' depends on them.

The vibrational motion in the plane of reaction (coordinate q^1) is coupled to that along the reaction coordinate q^2 via a constant of the motion, α_2 . The remaining motions of the complex, described by the ψ_3 -equation, are dynamically uncoupled from these two.

The resemblance of Eq. (26) to the Cartesian result (24) is increased by introducing α_1' , α_2' and κ' :

$$\alpha_1' = \alpha_1 - \alpha_3 - \alpha_2/q_0^1{}^2 \quad (28)$$

$$\alpha_2' = \alpha_2/q_0^1{}^2 \quad (29)$$

$$\kappa'(\alpha_2') \equiv \kappa(\alpha_2) \quad (30)$$

where q_0^1 is the value of q^1 at the saddle-point. Equation (26) becomes:

$$k_{\text{rate}} = \frac{kT}{h} e^{-\Delta U/kT} \frac{Q_3^\ddagger}{Q_0} \int_{\alpha_2} \left[\sum_{\alpha_1'} e^{-\alpha_1'/kT} \left\langle \frac{q_0^1{}^2}{q_1^2} \right\rangle \right] \kappa'(\alpha_2') e^{-\alpha_2'/kT} d\alpha_2'/kT \quad (31)$$

The transition of (31) to (24) may be seen by studying the behavior of the former in the region where the curvature of each coordinate curve near the saddle-point is small. The curvature of the q^1

coordinate curve is already zero. The curvature of the q^2 curve passing through the saddle-point is equal to the reciprocal of the radius vector there, i. e., to the value of $1/q^1$ for that curve. When q^1 is very large, q^1 undergoes only small fractional variations during any typical motion of the activated complex, and may be replaced in (31) by its value at the saddle-point, q_0^1 . Similarly, in the ψ_1 -equation, the a_2/q^{1^2} becomes $a_2/q_0^{1^2}$.

Then, a_1 becomes an eigenvalue of the ψ_1 -equation and, also, the sum in (31) becomes independent of a_2 . One obtains:

$$k_{\text{rate}} \xrightarrow{q_0^1 \rightarrow \infty} \frac{kT}{h} \frac{Q^\ddagger}{Q} e^{-\Delta U/kT} \int_{\alpha_2'}^{\alpha_2''} \kappa'(a_2') e^{-a_2'/kT} da_2'/kT \quad (32)$$

where Q^\ddagger equals $Q_3^\ddagger \sum_{\alpha_1} \exp(-\alpha_1/kT)$. It is the partition function of the activated complex for all coordinates but the reaction coordinate. Eq. (32) is in fact identical with (24).

In Appendix II it is also shown that the separated wave equations become those for the Cartesian case. This reduction and that given below for Example 3 can presumably also be used to suggest physically motivated approximations in (31) to simplify the integration-summation when the curvature consequences of the metric in the vicinity of the saddle-point are slight.

We conclude this section with some remarks on the use of Eq. (22) to calculate k_{rate} . For this calculation it is convenient to introduce α_1' defined above (it equals $\alpha_1 - \alpha_3$) and to note that da_1 can be replaced by da_1' . Eq.

(22) may then be summed over the discrete values of a_3 , yielding:

$$k_{\text{rate}} = \frac{kT}{h} e^{-U/kT} Q_3^\ddagger \int_{a_1'} \sum_{a_2} \kappa(a_2) e^{-a_1'/kT} da_1'/kT \quad (33)$$

Noting that for any given value of a_1' the solution of the ψ_1 -equation yields the allowed values of a_2 , κ may be calculated for these a_2 's, summed as in (33), and finally the latter may be integrated. For systems in which almost all of the activated complexes are formed in their lowest q^1 -vibrational states the first term in the sum suffices.

Example 3. Elliptic Cylinder Coordinates.

This coordinate system contains an added parameter, d , and therefore offers a somewhat more flexible choice in matching the separable and nonseparable energy surfaces over a larger distance from the saddle-point. When $2d$, the distance between the foci of the confocal ellipses vanishes, the coordinate curves degenerate into those for the circular cylinder system and (34) and (35) become identical with (25) and (26).

Coordinates q^1 and q^2 are introduced. They equal $(r_1 + r_2)/2$ and $(r_1 - r_2)/2d$, where r_1 and r_2 are the distances of a point in the plane to the two foci.

The matrix of $\phi_{\mu\nu}$'s is:¹⁶

$$\begin{pmatrix} 1 & -1/(q^1{}^2 - d^2) & -1 \\ d^2 & 1/(1 - q^2{}^2) & -d^2 \\ 0 & 0 & 1 \end{pmatrix} \quad (34)$$

As a reaction coordinate one may select a hyperbola or the arc of ellipse; q^r then becomes q^1 and q^2 , respectively. We consider the $r = 2$ case first.

(a) Reaction coordinate along arc of ellipse:

When the potential energy surface, plotted in mass-weighted coordinates, is symmetrical about the activated complex region, the saddle-point will occur on the major or minor axis of the ellipse, i.e., at $q^2 = \pm 1$ or 0 , respectively.

The quantities $\phi\phi^{21}$, $\phi\phi^{22}$, $\phi\phi^{23}$ equal $-(q^1{}^2 - d^2)^{-1}$, 1 and 0 , respectively. Accordingly, only the choice of $\alpha_k = \alpha_3$ is forbidden

in Eq. (21). We take $a_k = a_2$ to show the approach of (21) to the Cartesian formula.

The ψ_3 -equation depends only on a_3 , which therefore has discrete values. In the ψ_1 -equation, $\sum_{a_1} \phi_{1v}$ equals $a_1 - a_3 - a_2 (q^1{}^2 - d^2)^{-1}$. For a preassigned a_2 , $a_1 - a_3$ therefore has discrete values. The ψ_2 -equation is to be solved to obtain κ . It contains $\sum_{a_1} \phi_{2v}$, i.e. $(a_1 - a_3)d^2 + a_2 (1 - q^2{}^2)^{-1}$. κ is seen to depend on $a_1 - a_3$ and on a_2 .

Introducing $a' = a_1 - a_3$ the expression for k_{rate} becomes

$$k_{\text{rate}} = \frac{kT}{h} e^{-\Delta U/kT} \frac{Q_3^\ddagger}{Q} \int_{a_2} \sum_{a_1} \kappa(a_2, a') e^{-a'/kT} \left\langle \frac{1}{q^1{}^2 - d^2} \right\rangle da_2/kT \quad (35)$$

where $Q_3^\ddagger = \sum_{a_3} \exp(-a_3/kT)$ and where the average, $\langle \rangle$, is defined in Eq. (27).

The approach of expression (35) to (24) can be seen by examining the behavior of (35) when the curvilinear effects of the metric are small near the saddle-point.

(b) Reaction coordinate along a hyperbola

For a symmetrical potential energy surface the saddle-point occurs on the transverse axis²² of the hyperbola, i.e. at $q^1 = d$. Since ϕ/ϕ^{11} , ϕ/ϕ^{12} and ϕ/ϕ^{13} equal $(1 - q^2{}^2)^{-1}$, $-d^2$ and 0, respectively, only the choice of $a_k = a_3$ is forbidden in (21). When the approach to the Cartesian case is investigated it is noted in Appendix II that d tends to zero. Thus, only the choice of $a_k = a_1$ is permissible for investigating the approach. For calculation of k_{rate} in general, however, $a_k = a_1$ or a_2 can be used. For brevity, a detailed investigation of the approach will be omitted.

Example 4. Parabolic Cylinder Coordinates

Because the symmetry of the two parabolic coordinates, it makes no difference which of the two is selected as reaction coordinate. If the potential energy surface is symmetrical about the activated complex region, the saddle-point occurs on the axis of the confocal parabolas.

Effect of Rotational Motion on k_{rate}

In calculations of reaction rate constants rotation-vibration interactions are normally neglected. They were omitted in the derivation of (21) and (22) by making some of the g^{rs} constant and, thereby, some of the $\phi_{\mu\nu}$ constant or zero. The influence of the interactions will now be considered for completeness. Although this neglect is normally quite justified, there are a number of related problems where their inclusion is a matter of some importance. For example, the rates of unimolecular dissociation are influenced by the centrifugal potential in the molecule. Calculations of the dependence of the dissociation rate on the energy of a decomposing molecule should allow for it.

In the first approximation a "diatomic approximation" may suffice. In the latter only the rotational-vibrational interaction associated with a rotation involving the two largest moments of inertia is considered and one may proceed as follows:

In this "diatomic approximation", the Schrodinger equation has a form permitting separation of variables according to the formalism described earlier. The wave equation is first separated into equations for the translational (center of mass), rotational and internal motions using this formalism. The equation for internal motion now contains a rotational constant of the motion, which appears in a centrifugal potential term. The sum of the potential energy and of this centrifugal potential has a saddle-point when the original potential energy function has one and when the centrifugal distortion is not too large. A suitable system of internal coordinates is then introduced to permit this effective potential energy surface to be approximated by a surface permitting separation of variables, as described previously. Thereby, the choice of the reaction coordinate will ^{now} depend on the rotational state of the activated complex. With this qualification in mind, Eqs. (21) and (22) again apply, but now the summation over the rotational α should be made only after the other summations and the integration have been performed.

A slightly more general approach would be to neglect the vibrational angular momentum as before and to treat the activated complex as a symmetric top. Although separation of rotational from internal motion does not fall within the previously described formalism, one can

easily effect the separation in a standard way. The separated equation for the internal motion contains rotational constants of the motion and can be treated as in the preceding paragraph. Once again, the summation over the rotational α 's in Eqs. (21) and (22) would be performed last.

Appendix I. Evaluation of $(\partial p_r / \partial a_k)_{\lambda}$.

We first note that when a set μ contains a single coordinate, q^r , Eq. (9) reduces to:

$$-\frac{\hbar^2}{2f_r} \frac{\partial}{\partial q^r} f_r \frac{\partial \psi_r}{\partial q^r} + X_r \psi_r = \sum_{\nu=1}^m \alpha_{\nu} \phi_{r\nu} \psi_r \quad (A1)$$

The semiclassical approximation for ψ_r is then derived in the standard way by letting ψ equal $\exp(i S^r/\hbar)$, with S^r expanded in a power series in \hbar :

$$S^r = S_0^r + \frac{\hbar}{i} S_1^r + \left(\frac{\hbar}{i}\right)^2 S_2^r + \dots \quad (A2)$$

Retention of only the leading term yields the classical expression

$$\frac{1}{2} \left(\frac{\partial S_0}{\partial q^r} \right)^2 + X_r = \sum_{\nu=1}^m \alpha_{\nu} \phi_{r\nu} \quad (A3)$$

S_0 is a function of q^r and of the α 's, and $\partial S_0 / \partial q^r$ is the momentum p_r conjugate to q^r . Hence, we have:

$$\frac{1}{2} p_r^2 + X_r(q^r) = \sum_{\nu=1}^m \alpha_\nu \phi_{r\nu}(q^r) \quad (A4)$$

We shall also need (A5), obtained by multiplying (9) by ψ_μ^* and integrating over dq^μ , a symbol for the product $\prod_{i=1}^n dq^{\mu_i}$.

$$\int \psi_\mu^* (H_\mu + X_\mu f_\mu) \psi_\mu dq^\mu = \sum_{\nu=1}^m \alpha_\nu \int \phi_{\mu\nu} f_\mu \psi_\mu^* \psi_\mu dq^\mu \quad (A5)$$

¶ Continuous variation of p_r at constant discrete quantum number λ will cause a continuous variation in some of the α_ν 's, and zero variation in the others. Since the α_ν 's enter the separated equations, some of the ψ_μ 's are continuously altered, with no change in number of nodes, while others are unaffected. On letting the α_ν and ψ_μ in each of these $m-1$ equations (A5) (with $\mu \neq r$) undergo their variations resulting from a change in $p_r, \delta p_r$, and noting that the differential operator is Hermitian,⁷ one finds:

$$\begin{aligned} & \int \delta \psi_\mu^* (H_\mu + X_\mu f_\mu - \sum \alpha_\nu \phi_{\mu\nu} f_\mu) \psi_\mu dq^\mu \\ & + \int \delta \psi_\mu (H_\mu + X_\mu f_\mu - \sum \alpha_\nu \phi_{\mu\nu} f_\mu) \psi_\mu^* dq^\mu \\ & = \sum_{\nu=1}^m \delta \alpha_\nu \int \phi_{\mu\nu} f_\mu \psi_\mu^* \psi_\mu dq^\mu \end{aligned}$$

Because of Eq. (9), the left-hand side vanishes for the exact wave function. Hence,

$$\sum_{\nu=1}^m \delta \alpha_{\nu} \int \phi_{\mu\nu} f_{\mu} \psi_{\mu}^* \psi_{\mu} dq^{\mu} = 0 \quad \mu \neq r \quad (\text{A6})$$

From Eq. (A4) one also obtains:

$$\sum_{\nu=1}^m \delta \alpha_{\nu} \phi_{r\nu} = p_r \delta p_r \quad (\text{A7})$$

On solving Eqs. (A6) and (A7) for $\delta \alpha_k$ in terms of δp_r by means of Cramer's rule one finds:

$$\delta \alpha_k = \frac{p_r \delta p_r \left\{ \sum_{\substack{P \\ \nu_{\mu} \neq k}} (-1)^P \left[\prod_{\mu \neq r} \int \phi_{\mu\nu} f_{\mu} |\psi_{\mu}|^2 dq^{\mu} \right] \right\} (-1)^{r+k}}{\sum_P (-1)^P \left[\prod_{\mu \neq r} \int \phi_{\mu\nu} f_{\mu} |\psi_{\mu}|^2 dq^{\mu} \right] \phi_{r,\nu_r}} \quad (\text{A8})$$

where P represents an even or odd permutation of the ν_{μ} ($i = 1$ to m) from the standard order $1, \dots, m$. By interchanging the order of operations in the denominator of (A8), it can also be written as

$$\int_{\mu \neq r} \sum_P (-1)^P \phi_{r,\nu_r} \prod_{\mu \neq r} (\phi_{\mu\nu} f_{\mu} |\psi_{\mu}|^2 dq^{\mu}) \quad (\text{A9})$$

If ϕ denotes the determinant of the $\phi_{\mu\nu}$, this integral becomes

$$\int \phi \prod_{\mu \neq r} f_{\mu} |\psi_{\mu}|^2 dq^{\mu}$$

Similarly, the numerator of (A8) becomes $p_r \delta p_r$ multiplied by such an integral with ϕ replaced by an $m-1 \times m-1$ cofactor namely, the cofactor of ϕ_{rk} in ϕ . Because of (10) this cofactor equals $\phi \phi^{rk}$. One thus finds with the aid of (18),

$$\delta \alpha_k = p_r \delta p_r (\psi', \psi')_{rk} / \int |\psi'|^2 \phi \prod_{\mu \neq r} f_\mu \prod_{i \neq r} a_i^i$$

We may thus conclude that $(\partial p_r / \partial \alpha_k)_\lambda$ equals the value used in the text.

Appendix II. Approach to the Cartesian Case

The curvature of a q^i - coordinate curve in the plane of reaction, $\kappa_{(i)}$, for any of the cylinder coordinate systems in Examples 1 to 4 equals $1/2 \left| \frac{\partial \log g_{ii}}{\partial q^j} / g_{jj}^{1/2} \right|$, where q^j is the other coordinate in the plane of reaction. Since the element of arc length along the q^j - coordinate curve is ds_j , where

$$ds_j = g_{jj}^{1/2} dq^j, \quad (\text{A11})$$

one can also write:

$$\kappa_{(i)} = \frac{1}{2} \left| \frac{\partial \log g_{ii}}{\partial s_j} \right| \quad (\text{A12})$$

The ψ_1 - equation, Eq. (A1) with r replaced by i , can be converted to a form more suited to the present proof. We first write $g^{1/2}$ as $(g_{ii} g_{jj} g_z)^{1/2}$, where g_z is the determinant of the g_{st} 's in the set $\mu = 3$. In the case of no dynamic coupling between the set $\mu = 3$ on the one hand and the other two coordinates q^i and q^j on the other, g_z is independent of q^i and q^j . In the numerator of (A1) f_1 is now multiplied by $(g^{1/2} \prod_{\mu \neq i} f_\mu) (g^{1/2} \prod_{\mu \neq i} f_\mu)^{-1}$. Eqs. (13) and (A11) are next used. One then notes from (11) g^{ii} and g^{jj} equal ϕ^{i1} and ϕ^{j1} , since i and j are one-dimensional sets. Since g_z , $\prod_{\mu \neq i} f_\mu$, and ϕ^{i1} commute with d/dq^i one finally obtains

$$\frac{d^2 \psi_1}{ds_1^2} + \kappa'_{(j)} \frac{d\psi_1}{ds_1} + \frac{2}{h^2} \phi^{i1} \left(X_1 + \sum_{\nu=1}^3 a_\nu \phi_{1\nu} \right) \psi_1 = 0 \quad (\text{A13})$$

where $\kappa'_{(j)}$ equals $\frac{1}{2} \partial \log g_{ii} / \partial s_j$, and so has the same magnitude as $\kappa_{(j)}$. An equation similar to (A13) obtains for ψ_j , with i and j merely interchanged.

For the curvilinear case to approach the Cartesian one several conditions must be fulfilled. (a) The curvatures $\kappa_{(i)}$ and $\kappa_{(j)}$ must become negligible in (A13). (b) $\phi^{i1} x_i$ in (A13) must tend to become a function of q^1 alone. (c) $\sum_{\nu} \phi^{i1} \phi_{i\nu} a_{\nu}$ in (A13) must become approximately constant over the relevant region of configuration space near the saddle-point.

We consider Examples 2 and 3 individually.

(i) Example 2. From (A11), (A12) and the known g_{ii} 's the limiting case of vanishing curvatures of the curves passing through a point occurs when q^1 tends to infinity. The term $\phi^{i1} \sum_{\nu} a_{\nu} \phi_{i\nu}$ is given by (28) and (29) for $i = 1$ and 2 , respectively, with q_0^1 replaced by q^1 . When q^1 has some large value, q_0^1 , this term becomes essentially a constant and so condition (c) above is fulfilled. Condition (b) is also fulfilled. Finally, the a_2 in (29) is the same as the one in (32) and the proof is complete.

(ii) Example 3. From Eqs. (A11), (A12) and the known g_{ii} 's one may find the conditions under which conditions (a) to (c) above are fulfilled. They correspond to large q^1 and relatively small d . This case then reduces to the circular cylinder case, namely Example 2, and will not be considered further. If the reaction coordinate is that in Example 3b, the choice $a_k = a_2$ is forbidden when d tends to zero. Thus, in that case a_k must be chosen as a_1 if one wishes to investigate the approach to the Cartesian case.

References

1. H. Eyring, J. Chem. Phys. 3, 107 (1935); E. Wigner, Trans. Faraday Soc. 33, 29 (1937); E. Wigner, Z. physik. Chem. B19, 203 (1932).
M. G. Evans and M. Polanyi, Trans. Faraday Soc. 31, 875 (1935), employ an argument based on the partition function for the imaginary frequency, a partition function normally derived for a rectilinear (i.e., Cartesian) vibrational coordinate. G. H. Vineyard, in J. Phys. Chem. Solids 2, 121 (1957), gives an elegant formulation for site-to-site motion in crystals. He assumes the reaction coordinate to be rectilinear.
2. In a classically based quasi-equilibrium treatment one considers dynamical properties of the system infinitesimally close to the (n-1) dimensional hypersurface in configuration space defining the properties of an activated complex. (The total number of coordinates in configuration space is n.)
In the quantum treatment, the implications of the uncertainty principle eliminate such considerations. One must employ instead a treatment based on the properties of the potential energy function over non-infinitesimal distances from the above hypersurface. In this case, however, the problem of separability of the equation of motion arises.
3. For example, the angular momentum of the complex gives rise to a centrifugal potential whose influence on the vibrational motion is usually, and justifiably, ignored. There are some instances, such as in bimolecular reactions of negligible activation energy, where it should be and has been included in literature calculations, as well as in those on the reverse unimolecular dissociation.

4. In some problems, as in the unimolecular reaction of vibrationally excited molecules, a local equilibrium between a hot molecule and the activated complex for its reaction is assumed instead. (E.g., R. A. Marcus and O. K. Rice, *J. Phys. Colloid Chem.* 55, 894 (1951); R. A. Marcus, *J. Chem. Phys.* 20, 359 (1952).)
5. R. A. Marcus, *J. Chem. Phys.* (to be submitted).
6. The vibrational angular momentum is neglected. (The internal coordinates are chosen to satisfy the Eckart conditions, however.)
See footnote 15, Ref. 7.
7. R. A. Marcus, *J. Chem. Phys.* 41, 000 (1964). Aug. 1 issue. The features which are matched are the tangent, the first curvature vector, the first curvature, and the force constant along each extremal path of ascent or descent to the saddle-point.
8. Quantum calculations: E. M. Mortensen and K. S. Pitzer, *Chem. Soc. (London) Spec. Publ.* 16, 57 (1962). Classical calculations: F. T. Wall, L. A. Hiller, Jr. and J. Mazur, *J. Chem. Phys.* 29, 255 (1958), *ibid* 35, 1284 (1961); N. C. Blais and Bunker, *ibid* 39, 315 (1963) and references cited therein.
9. S. Glasstone, K. J. Laidler and H. Eyring. *Theory of Rate Processes.* McGraw-Hill Book Co., Inc. (1940).
10. Calculations are in progress by J. Lane and R. A. Marcus for $n=2$.
11. E.g., W. Pauli, Jr. *Handbuch der Physik*, 5, 39 (1958).
12. E.g., A. J. McConnell, *Applications of Tensor Calculus*, Dover Publications, Inc., New York (1957).
13. R. A. Marcus, *J. Chem. Phys.* 41, 000 (1964). Aug. 1 issue. Appendix II there shows how the formalism embodied

in the equations of the present paper, (5) to (13), includes the influence of rotation in the case of a diatomic rotating-vibrating molecule.

14. P. G. Stäckel, Habilitationsschrift, Halle,^{Germany} (1891); Ann. Mat. Pure Appl., Ser. 2A, 25, 55 (1897).
15. L. P. Eisenhart, Ann. Math. 35, 284 (1934).
16. cf. P. M. Morse and H. Feshbach, Methods of Theoretical Physics, McGraw-Hill Book Co., Inc. New York (1953), p. 655 ff.

17. This procedure is a generalization of the customary one of introducing the harmonic approximation for the potential energy surface.

The latter approximation corresponds in fact to the reaction coordinate curve being a straight line in n-dimensional space and to the remaining coordinate curves lying in a hyperplane. Normal to this hyperplane is the reaction path in this mass-weighted configuration space, a path which is distinct from the reaction coordinate. They are co-tangential at the saddle-point.

18. I.e., the W.B.K. expression, such as that used by R. P. Bell, Proc. Roy. Soc. (London) A148, 241 (1935) or that in Ref. 20.
19. The kinetic energy in classical mechanics is $\frac{1}{2} \sum_{i,j=1}^n g_{ij} \dot{q}^i \dot{q}^j$, so that the momentum conjugate to q^i , p_i , is $\sum_{j=1}^n g_{ij} \dot{q}^j$. In the systems being considered g^{ij} vanishes when i and j belong to different sets. Since the reaction coordinate is a one-dimensional separable set g^{ir} vanishes when $i \neq r$. It then follows that g_{ir} also vanishes for $i \neq r$ and g_{rr} equals $1/g^{rr}$. Hence, p_r equals \dot{q}^r/g^{rr} . Eq. (11) then shows that $p_r = \dot{q}^r/\rho^{r1}$ since $h_r = 1$ and there is only one g^{rj} , namely g^{rr} .

20. R. A. Marcus, J. Chem. Phys. (to be submitted). The discussion is based on some results contained in a recent book by J. Heading, An Introduction to Phase-Integral Methods, Methuen & Co., Ltd., London (1961).
21. E. g., R. E. Weston, Jr., J. Chem. Phys. 31, 892 (1959).
22. A. B. Grieve, Analytical Geometry (G. Bell and Sons, Ltd. 1948), p.85.
23. e.g., O. Schreier and E. Sperner. Introduction to Modern Algebra and Matrix Theory. Chelsea Publishing Co., New York 2nd Ed. (1959), p.101,98.
24. This expression is deduced from the equation for the curvature in generalized coordinates. See, for example, Eqs. (16), (18) and (19b) of Reference 7, with N and i replaced now by i and j, respectively. The cited value of $\kappa_{(i)}$ follows at once from these equations, when one notes that all components of the curvature vector vanish except those in the plane of reaction.