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A Generalization of Activated Complex Theory of Reaction Rates

II. Classical Mechanical Treatment*

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In its usual classical form activated complex theory assumes a particular expression for the kinetic energy of the reacting system one associated with a rectilinear motion along the reaction coordinate. The derivation of the rate expression given in the present paper is based on the general kinetic energy expression. A rate equation of the customary form is obtained:

$$k_{rate} = \frac{kT}{h} e^{-(F^{\ddagger} - F^{r})/kT}$$

where $F^{\ddagger}$ is the free energy of a system constrained to exist on a hyper-surface in n-dimensional space and F^r is the free energy of the reactants. The usual derivation is then reinterpreted, in terms of geodesic normal coordinates, to be somewhat more general than it appears.

Normally, rotation-vibration interaction is neglected, as in the above derivation, although not in treatments of some special reactions in the literature for which the centrifugal potential is important. A derivation is given which includes the influence of this centrifugal potential and which omits coriolis effects.

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DISCLAIMER

Introduction

A number of derivations of the activated complex theory equation for chemical reaction rates have been published.[1] Several assumptions normally made in the classical mechanical form of the theory are the following:

1. For reaction to occur some n-1 dimensional hypersurface in the n-dimensional configuration space must be crossed. (The hypothetical system constrained to exist on this surface is the "activated complex". The surface will be called the "reaction hypersurface".)
2. The probability of finding the system in any part of the 2 n-dimensional phase space on the reactants' side of the above surface is that calculated from equilibrium statistical mechanics.
3. A system striking the above hypersurface has unit probability of crossing it and recrossings can be neglected. Thereby, the transmission coefficient is unity.
4. The kinetic energy along the reaction coordinate has a very simple form, $p^2/2\mu$, where p is the momentum conjugate to this coordinate and μ is a constant, and there are no cross-terms with p in the total kinetic energy expression.[2]

In addition, the Born-Oppenheimer approximation is normally employed. Sometimes this approximation breaks down, the reaction becoming quantum mechanically nonadiabatic. The rate is then occasionally calculated with the aid of the Landau-Zener equation, and some approximations are contained therein.[3]

In the present paper assumption 4 is removed. Assumption 1 is later weakened by permitting the internal motions of the complex to depend on rotational constants of the motion. Removal of assumption 4 leads, surprisingly perhaps, to a rate equation formally similar to the usual one of activated complex theory. The reason for this behavior is described later: it is shown that if one reinterprets the coordinates employed in the usual derivation as "geodesic normal coordinates" no approximation in "assumption" 4 was actually made. The subsequent shortcomings of such coordinates for purposes of comparing with a quantum mechanical formulation are then noted. However, assumption 4 has now been removed.

The present paper is confined to a classical mechanical description. A related quantum mechanical treatment was given earlier.[4] While the latter was more general than the classical treatment in that quantum effects were included, it was also less general in that the assumption of separability of the reaction coordinate was made for practical convenience in the quantum treatment but not in the classical one. The reason for this difference has been described previously. To be sure, the assumption of separability is less drastic than formerly, because of the availability of a recently devised local approximation of "nonseparable" potential energy surfaces by surfaces permitting separation of variables.[5]

One application of the present paper has been made elsewhere to electron transfer reactions.[6] It can also be applied to other reactions in solution for which many degrees of freedom are involved in the definition of the activated complex and for which the usual saddle-point definition[1,2] need no longer suffice.

The Hamiltonian and Other Properties

The line element in mass-weighted configuration space, ds, is given by (1).

$$ds^2 = \sum_{k=1}^{n} m^k (dx^k)^2 = \sum_{i,j=1}^{n} g_{ij} \; dq^i \, dq^j \tag{1}$$

where the x^k are space-fixed Cartesian coordinates of the atoms ($m^{3r} = m^{3r+1} = m^{3r+2}$ is the mass of the r'th atom). The q^i are generalized coordinates, and g_{ij} is a symmetric, covariant second order tensor,[7] given by (2):

$$g_{ij} = \sum_{k=1}^{n} m^k \frac{\partial x^k}{\partial q^i} \frac{\partial x^k}{\partial q^j} \tag{2}$$

The contravariant tensor conjugate to g_{ij} is g^{ij}:

$$g^{ij} = \sum_{k=1}^{n} \frac{1}{m^k} \frac{\partial q^i}{\partial x^k} \frac{\partial q^j}{\partial x^k} \tag{3}$$

$$\sum_{j=1}^{n} g^{ij} g_{jk} = \sum_{j=1}^{n} g_{kj} g^{ji} = \delta^i_k \tag{4}$$

where δ^i_k is 0 or 1 according as $i \neq k$ or $i = k$.

The kinetic energy T equals $\frac{1}{2}(ds/dt)^2$ and so is given by (5) in terms of the generalized velocities $\dot{q}^i$.[8]

$$T = \tfrac{1}{2} \sum_{i,j=1}^{n} g_{ij} \, \dot{q}^i \, \dot{q}^j \tag{5}$$

Some of the q^i's are usually rotations, with the result that many of the g_{ij} are then neither diagonal nor constant. Since the generalized momentum p_i equals $\partial(T-U)/\partial\dot{q}^i$, where $U(q^1,\ldots q^n)$ is the potential energy, p_i is given by (6).[9] From (4) to (6), Eq. (7) is obtained for H, the Hamiltonian of the system.[10]

$$p_i = \sum_{j=1}^{n} g_{ij}\,\dot{q}^j \tag{6}$$

$$H = \tfrac{1}{2}\sum_{i,j=1}^{n} g^{ij}\,p_i p_j + U(q^1,\ldots q^n) \tag{7}$$

We shall also need the line element, ds, in ordinary configuration space:

$$ds^2 = \sum_{k=1}^{n}(dx^k)^2 = \sum_{i,j=1}^{n} a_{ij}\,dq^i\,dq^j \tag{8}$$

where a_{ij} is a covariant tensor. The contravariant tensor a^{ij} is conjugate to it. Both are defined in (9):

$$a_{ij} = \sum_{k=1}^{n}\frac{\partial x^k}{\partial q^i}\frac{\partial x^k}{\partial q^i}\ ; \quad a^{ij} = \sum_{k=1}^{n}\frac{\partial q^i}{\partial x^k}\frac{\partial q^j}{\partial x^k}\ , \tag{9}$$

$$\sum_{j=1}^{n} a^{ij}\,a_{jk} = \sum_{j=1}^{n} a_{kj}\,a^{ji} = \delta^i_k \tag{10}$$

We shall make use of some results on determinants. Because of the product rule, (11) follows from (2), and (12) from (9).[11]

$$\det_{i,j=1}^{n} g_{ij} = \prod_{k=1}^{n} m^k\left(\det_{i,j=1}^{n}\frac{\partial x^i}{\partial q^j}\right)^2 \tag{11}$$

$$a = \det_{i,j=1}^{n} a_{ij} = \left(\det_{i,j=1}^{n}\frac{\partial x^i}{\partial q^j}\right)^2 \tag{12}$$

The volume element in mass-weighted configuration space and that in ordinary configuration space will be denoted by $d\tau$ and dV, respectively:[12]

$$d\tau = (\det g_{ij})^{\frac{1}{2}} \prod_{i=1}^{n} dq^i \qquad (13)$$

$$dV = (\det a_{ij})^{\frac{1}{2}} \prod_{i=1}^{n} dq^i = (\det_{i,j=1}^{n} \frac{\partial x^i}{\partial q^j}) \prod_{i=1}^{n} dq^i \qquad (14)$$

Because of (11), one obtains (15) from (13).

$$d\tau = \left[\prod_{k=1}^{n} (m^k)^{\frac{1}{2}}\right] \det \frac{\partial x^i}{\partial q^j} \prod_{i=1}^{n} dq^i = \left[\prod_{k=1}^{n} (m^k)^{\frac{1}{2}}\right] dV \qquad (15)$$

The area element of a coordinate hypersurface on which q^N is constant will be denoted by $d\sigma$ and by dS for mass-weighted and ordinary configuration space, respectively. These area elements are the volume elements in an n-1 dimensional space in which dq^N is zero.[13] Hence,

$$d\sigma = (\det_{i,j\neq N} g_{ij})^{\frac{1}{2}} \prod_{i\neq N} dq^i \qquad (16)$$

$$dS = (\det_{i,j\neq N} a_{ij})^{\frac{1}{2}} \prod_{i\neq N} dq^i \qquad (17)$$

Since gg^{NN} and $\det_{i,j\neq N} g_{ij}$ are each the cofactor of g_{NN} in g, they are equal. From (16) one then obtains (18). Eq. (19) follows similarly from (17), since both aa^{NN} and $\det_{i,j\neq N} a_{ij}$ are the cofactor of a_{NN} in a.

$$d\sigma = (gg^{NN})^{\frac{1}{2}} \prod_{i\neq N} dq^i \tag{18}$$

$$dS = (aa^{NN})^{\frac{1}{2}} \prod_{i\neq N} dq^i \tag{19}$$

Derivation of the Rate Equation for a Reaction Hypersurface Dependent on Coordinates Alone

When the "reaction hypersurface" depends on the coordinates alone, it is independent, thereby, of any constants of the motion. Otherwise, the latter would appear as parameters in the equation of the hypersurface. The equation of this hypersurface, S, may be written as

$$f(q^1,\ldots,q^n) = 0 \qquad \text{(on S)}$$

A choice of coordinates can be made so that S is a coordinate hypersurface for one of them, q^r. Thus, q^r is constant on S, and can be taken as zero on it. This surface will be a q^r- coordinate hypersurface both in mass-weighted and in ordinary configuration space.

The reaction rate is the net rate at which systems cross S. It can be computed under the equilibrium assumption for the reactants as follows: The probability that a system in equilibrium with the reactants will lie in a volume element of phase space, $\prod_{i=1}^{n} dq^i dp_i$, will be denoted by $\rho \prod_{i}^{n} dq^i dp_i$, where ρ is the equilibrium phase space density:

$$\rho = e^{-H(p,q)/kT} \Big/ \iint e^{-H(p,q)/kT} \prod_{i=1}^{n} dq^i dp_i \tag{20}$$

On dividing the above probability by dq^r and multiplying by $\dot{q}^r$, the probability that the reacting system will cross the element $\prod_{i\neq r} dq^i$ of the hypersurface S in unit time is found to be $(\int \rho \dot{q}^r \prod_{i=1}^{n} dp_i) \prod_{i \neq r} dq^i$, where the integration is over all p_i such that only passages from the reactants' side of S to the products' side are counted. The rate constant is then obtained by integrating over the coordinates.

$$k_{rate} = \int \rho \; \dot{q}^r \prod_{i=1}^{n} dp_i \prod_{i \neq r} dq^i \tag{21}$$

By definition of a rate constant of a homogeneous reaction (it has units of moles/volume and time) the q-integration in (21) is such that three translational coordinates of the activated complex are integrated over a unit volume. For a heterogeneous reaction the integration in (21) is such that the two translational coordinates of the activated complex parallel to the interface of the two phases are integrated over a unit area of the interface.[14] In the denominator of (20) the integration over the translational coordinates of each reactant is over unit volume.

On one side of S (the reactants', say), $\dot{q}^r$ is negative and on the other side it is positive. Accordingly, in order to count only passages from one first side of S to the other, the integration in (21) is such that $\dot{q}^r$ is confined to the interval $(0, +\infty)$.

According to Footnote 10, $\dot{q}^r$ is given by

$$\dot{q}^r = \sum_{j=1}^{n} g^{rj} p_j \tag{22}$$

For any given value of $\dot{q}^r$, (22) represents the equation of a hyperplane in momentum space. Integration in (21) may therefore be performed as follows: For any given value of $(q^1,\ldots,q^n)$ the p_i's are integrated over the infinite half-space in momentum space, corresponding to all variations in p_i subject to $\sum_{j=1}^{n} g^{rj} p_j$ lying between zero and infinity.

By integrating p_r from $-\sum_{j\neq r} g^{rj}\, p_j/g^{rr}$ to ∞ and by integrating the remaining p_j from $-\infty$ to ∞ this integration can be performed. During a subsequent integration over all q^i other than $i=r$, q^r is kept at the value zero. Since $\dot{q}^r$ is $\partial H/\partial p_r$, $\dot{q}^r \exp(-H/kT)$ equals $-kT\, \partial e^{-H/kT}/\partial p_r$. The p_r integration yields (23):

$$k_{rate} = \frac{kT}{h}\, e^{-(F^{\ddagger}-F)/kT} \tag{23}$$

where
$$e^{-F^{\ddagger}/kT} = \int e^{-H^{\ddagger}(p,q)/kT} \prod_{i\neq r} dq^i dp_i/h^{n-1} \tag{24}$$

$$e^{-F/kT} = \int e^{-H(p,q)/kT} \prod_{i=1}^{n} dq^i dp_i/h^n \tag{25}$$

and $H^{\ddagger}$ is given by (26). It is the value of H when $q^r = \dot{q}^r = 0$. Thus, it is the value of H for a system constrained to exist on the hypersurface of S.

$$H^{\ddagger} = T^{\ddagger} + U^{\ddagger} \tag{26}$$

where

$$U^{\ddagger} = U(q^1,\ldots,q^n) \text{ at } q^r = 0 \tag{27}$$

$$T^{\ddagger} = \tfrac{1}{2} \sum_{i,j\neq r} g_{ij}\, \dot{q}^i \dot{q}^j = \tfrac{1}{2} \sum_{i,j\neq r} g^{ij^{\ddagger}}\, p_i p_j \tag{28}$$

and

$$g^{ij^{\ddagger}} = \sum_{i,j\neq r} \left[g^{ij} - g^{ir} g^{jr} (g^{rr})^{-1} \right] \tag{29}$$

The quantity $g^{ij^{\ddagger}}$ is easily shown to be conjugate to g_{ij} on a subspace for which $dq^r = 0$, i.e., on the hypersurface, S.

$$\sum_{j\neq r} g^{ij^{\ddagger}} g_{jk} = \sum_{j\neq r} g_{kj} g^{ji^{\ddagger}} = \delta^i_k \; (i,k\neq r) \tag{30}$$

$F^{\ddagger}$ is the free energy of the constrained system and F is the free energy of the unconstrained reacting system. In both free energies and in all subsequent free energy expressions the usual product of factorials, which corrects for indistinguishability of like particles, is omitted for brevity. These factors cancel in computing (23).

In passing, we note that Eq. (23) has been obtained without introducing assumption 4.

Integration over the momenta in (24) and (25) can readily be performed. One obtains:

$$e^{-F^{\ddagger}/kT} = (2\pi kT)^{\frac{n-1}{2}} \int e^{-U^{\ddagger}/kT} d\sigma/h^{n-1} \tag{31}$$

$$e^{-F/kT} = (2\pi kT)^{\frac{n}{2}} \int e^{-U/kT} d\tau/h^{n} \tag{32}$$

where $d\sigma$ is given by (16) and $d\tau$ by (13).

On introducing an effective mass $m^{\ddagger}$ defined in the next section, the expression for the rate constant becomes:

$$k_{rate} = (kT/2\pi)^{\frac{1}{2}} \int e^{-U^{\ddagger}/kT} (m^{\ddagger})^{-\frac{1}{2}} dS \Big/ \int e^{-U/kT} dV \tag{33}$$

where dV is given by (14) and dS by (17).

An Effective Mass

An effective mass, $m^{\ddagger}$, for motion normal to S in ordinary n dimensional configuration space may be defined in several ways. A definition suited to our purpose is the following: When the momentum $\underset{\sim}{p}$ is normal to S in this ordinary configuration space the proportionality factor of $p^2/2$ in the kinetic energy will be designated by $1/m^{\ddagger}$. To evaluate $m^{\ddagger}$, one may proceed thus:

The covariant components of a vector $\underset{\sim}{\nu}$ of unit length (magnitude) normal to the q^r-coordinate hypersurface S in this space are equal to[15] $\nu_i = \delta_i^r (a^{rr})^{-\frac{1}{2}}$. The covariant components of $\underset{\sim}{p}$, p_i, are therefore equal to $\delta_i^r\, p\, (a^{rr})^{-\frac{1}{2}}$, where p is the magnitude of $\underset{\sim}{p}$. On noting that the kinetic energy is given by the first term in (7) and on introducing the above values for the p_i's, the kinetic energy is found to equal $g^{rr}p^2/2a^{rr}$. Hence, we have

$$m^{\ddagger} = a^{rr}/g^{rr} \tag{34}$$

Integration over External Coordinates

In a dilute gas an activated complex may be regarded as an isolated particle. In a liquid or dense gas its motions may be strongly coupled to those of the surrounding molecules. In the latter case it will be useful to consider as the activated complex a macroscopic subsystem, near the center of which is the actual reactant or pair of reactants and on the boundary of which the correlation of the motion of the solvent molecules with those of the reactants is negligible. This subsystem is regarded as imbedded in the remainder of the infinite (or practically infinite) system. For homogeneous reactions rigid translations or rotations will later be performed on the subsystem, and the solvent molecules of the remaining part will be permitted to continuously adjust themselves. For heterogeneous systems rigid translations of the macroscopic activated complex parallel to the interface will be performed with a similar adaptation of the remaining molecules occurring.

The activated complex of a homogeneous reaction in a gas or liquid, defined above, has as coordinates three translations (x, y, z), two rotations of an axis fixed in the complex (θ, ϕ), and n-5 other coordinates, which will be called the internal coordinates of the complex, though one of them (rotation about the body-fixed axis) has a property analogous to the five "external" ones: The potential energy of the entire system is invariant to changes in the five external coordinates.

In the case of a heterogeneous reaction on a uniform interface the potential energy function for the activated complex is invariant to the two Cartesian coordinates, x and y, parallel to the interface of the two phases.[14] Presumably, such a case occurs in electrochemical electron transfers to a good approximation when the reactant is not adsorbed. In reactions involving localized adsorption on perfect crystals the potential energy is a periodic function of x and y. For any heterogeneous reaction the remaining n-2 will be called the internal ones of the activated complex, though in the particular case of a nonuniform surface, $U^{\ddagger}$ and q^r below depend on <u>all</u> n coordinates.

The integral appearing in the denominator of (33) is evaluated for a system where the reactants are far apart, when there is more than one of them, or far from the interface in the heterogeneous reaction. The function U in this integral is independent of the three translations of the center of mass of each reactant, which will be called the external coordinates for the denominator of (33). (However, U is also independent of some of the other coordinates, of course.)

Since the properties of the reaction hypersurface depend only on the internal coordinates they can be selected so that the coordinate q^r is one of them.

The reduced mass $m^{\ddagger}$ is shown in Appendix I to be independent of the values of the external coordinates. It normally is a function of the internal coordinates, though it is a constant in special cases, as discussed later. The area element dS is shown in Appendix II to be a product of a function of the external coordinates alone and of a function of the internal coordinates alone, the latter denoted by $R^2 dS_{int}$ for bimolecular reactions and by dS_{int} for homogeneous unimolecular reactions or for heterogeneous reactions, as discussed in the Appendix.

$$\begin{pmatrix}\text{homogeneous}\\ \text{bimolecular}\end{pmatrix} \quad dS = \sin\theta \, d\theta \, d\phi \, dx \, dy \, dz \, R^2 \, dS_{int} \tag{35}$$

$$\begin{pmatrix}\text{homogeneous}\\ \text{unimolecular}\end{pmatrix} \quad dS = \sin\theta \, d\theta \, d\phi \, dx \, dy \, dz \, dS_{int} \tag{36}$$

$$(\text{heterogeneous}) \quad dS = dx \, dy \, dS_{int} \tag{37}$$

where θ and ϕ define a body-fixed axis of the complex, R is the distance of two atoms or any two points of the complex on this axis, and x, y, z have been defined earlier. In the computation of dS_{int} in (35) the two atoms or points are constrained so that one is fixed on the cited body-fixed axis and the other can move only along that axis. The two points can be the centers of mass of each reactant, for example (Appendix II). In the compution of the dS_{int} of (37) one point of the complex is constrained to move along any fixed line normal to the xy plane (parallel to the solid-liquid interface. This point can be the center of mass of the reactant.

Similarly, the volume element dV in (33) can be shown to be the product of volume elements $\prod_a dx_a \, dy_a \, dz_a$ for the external coordinates of all reactants a and of dV_{int}, the volume element of all remaing coordinates. (There is only one term in $\prod_a$ when the reaction is unimolecular, of course.) These remaining coordinates are cordinates in a space where the center of mass of each reactant is fixed and where the reactants are far apart.

Integration may now be performed over the external coordinates in the numerator and denominator of (33). One obtains

(bimolecular homogeneous) $$k_{rate} = (8\pi kT)^{\frac{1}{2}} \int R^2 (m^{\ddagger})^{-\frac{1}{2}} e^{-U^{\ddagger}/kT} dS_{int}/Q \tag{38}$$

(unimolecular homogeneous, or uniform heterogeneous) $$k_{rate} = (kT/2\pi)^{\frac{1}{2}} \int (m^{\ddagger})^{-\frac{1}{2}} e^{-U^{\ddagger}/kT} dS_{int}/Q \tag{39}$$

where constraints on the numerator integration have just been described and where Q is given by (40),

$$Q = \int e^{-U/kT} dV_{int} \tag{40}$$

It is the configurational integral of the reactants when they are far apart. Integration in Q is subject to the constraint that a point on each reactant (e.g., its center of mass) is held fixed, and thus is over the volume V_{int} of some n-3N dimensional internal coordinate space where N is the number of reactants. For a heterogeneous reaction on a nonuniform interface, dS_{int} in (39) should be replaced by dx dy dS_{int}; x and y vary over a unit area of interface. In either case, k_{rate} is the reaction rate per unit area of interface per unit concentration of the reactant. It has units of cm sec^{-1}, for example.

Some Special Cases of Eqs. (38) and (39)

In the simple collision theory the q^r-reaction hypersurface is taken to be one of constant separation distance between the centers of mass of each reactant in the bimolecular reaction, which will be denoted by R, the collision diameter. The quantity $m^{\ddagger}$, it can shown, is then a constant, and in fact equal to μ, the reduced mass for the two reactants. Since R is now constant over S it too can be extracted from the integral in (38). Integration then leads to the simple collision theory expression $(8\pi kT/\mu)^{\frac{1}{2}} R^2 \exp(-\Delta U/kT)$, since the area element in the numerator is now the same as the volume element in the denominator.

In an analogous simple collision theory for unimolecular heterogeneous reactions, the q^r- reaction hypersurface is taken to be a plane parallel to the interface of the two phases. In that case $m^{\ddagger}$ can again be shown to be a constant, the mass of the reactant, m, and the simple heterogeneous collision theory expression is obtained, $(kT/2\pi m)^{\frac{1}{2}} \exp(-\Delta U/kT)$, since the area element in the numerator and the volume element in the denominator are equal.

Another special case of (38) and (39) obtains when the q^r- reaction hypersurface can be chosen to be a hyperplane in the internal coordinate space of the activated complex. (This hyperplane passes through the saddle-point, when the latter exists, and is normal to the tangent of a line of steepest

ascent to the saddle-point drawn in internal coordinate space.)
The hyperplane approximation has been used by Vineyard[1] in his calculation of the rate of diffusion of an atom from one site to a neighboring one in a crystal. His results are derivable from (39).
This hyperplanar approximation is often made in the usual activated complex theory, by using normal coordinate analyis and neglecting vibration-rotation interaction.

Case where Reaction Hypersurface Depends on Rotational Constants of the Motion

In some reactions, the equation of the reaction hypersurface may depend on constants of the motion, in particular on the angular momentum. Several examples are some unimolecular dissociations, radical recombinations,[16] and ion-molecule reactions.[17] For example, the reactants in the two latter reactions have been treated as two particles which, in the activated complex, have their mutually attractive force balanced by their centrifugal force. The attraction was attributed to induced dipole-induced dipole forces in the recombination and to ion-induced dipole forces in the ion-molecule system. The centrifugal force was calculated by treating the pair of reactants as a "diatomic" activated complex.

The above treatments were based on the assumption that the reaction hypersurface is the set of coordinates for which the attractive force equals in magnitude the repulsive centrifugal force between the two particles. This set depends on the angular momentum. In these and other reactions this "diatomic" approximation is readily imposed on the treatment of the previous section, when an angular momentum dependence of the reaction hypersurface is to be considered: For a given angular momentum of the complex in any infinitesimal range the contribution to the overall reaction rate can be calculated. One may then integrate over all angular momenta. The result will emerge as a special case of the "symmetric top" approximation treated below, and its derivation will be omitted for that reason. (The derivation parallels the one below, but the angle ψ and the conjugate momentum p_ψ are omitted, and the "bar" subspace is one dimension larger.)

If the "diatomic" approximation is inadequate, in that the value of a third principal moment of inertia of the complex changes during reaction, a somewhat better approximation can be obtained by treating the complex as a symmetric top and including the dependence of the reaction hypersurface on the magnitude of the angular momentum p_{rot} as before, and on the component of p_{rot} along the symmetry axis, p_{ψ}. If the vibrational angular momentum is ignored the kinetic energy of the complex is the sum of terms from the three translations of the center of mass, from the rotations, and from the remaining 3 n-6 internal coordinates. The rotational energy of a symmetric top complex is given by (41),[18] The three principal moments of inertia of the complex are A, A and C.

$$T_{rot} = \frac{p_{rot}^2}{2A} + \frac{p_{\psi}^2}{2}\left(\frac{1}{C} - \frac{1}{A}\right) \tag{41}$$

Since p_{rot} and p_{ψ} are constants of the motion, and since A and C depend on the internal coordinates T_{rot} acts as a centrifugal potential, thereby affecting the reaction hypersurface by an amount depending on p_{rot} and p_{ψ}.

The reactions of present interest for which the hypersurface may depend significantly on the angular momentum are gas reactions. In this case, it is convenient to transform the Cartesian coordinates of the atoms in the complex x^k into generalized coordinates q^i, three of which are the translations of the center of mass of the activated complex. Another three are selected to be the Eulerian angles (θ, ϕ and ψ) defining the orientation of the principal axes, and the remaining n-6 will be called the internal coordinates of the activated complex. The line-element in mass-weighted space is given by (1).

The internal coordinates may be chosen so as to satisfy the Eckart conditions,[19] lessening thereby the vibrational angular momentum. The residual vibrational angular momentum will be neglected, however, an approximation which corresponds to setting g^{ij} equal to zero when i is one of the internal coordinates and j is one of the Eulerian angles. Correspondingly, one can show, g_{ij} also vanishes then for these choices of i and j. Independently of this approximation the usual expression for the kinetic energy in terms of the $\dot{q}^i$'s or p_i's shows that g^{ij} and g_{ij} also vanish when i is a translation of the center of mass and j is an orientational or an internal coordinate.

It will be convenient to choose the internal coordinates in such a way that one of the coordinates, q^r, is constant on the reaction hypersurface. If the internal coordinates are denoted by q^1 to q^{n-6} their choice may depend on p_{rot} and p_ψ, since the hypersurface and, thereby, q^r depend on p_{rot} and p_ψ. Thus, we have:

$$q^i = q^i(x^1,\ldots x^n) \qquad i = n-5 \text{ to } n \tag{42}$$

$$q^i = q^i(x^1,\ldots x^n, p_{rot}, p_\psi) \qquad i = 1 \text{ to } n-6 \tag{43}$$

This definition of q^1 to q^{n-6} would not necessarily be a consistent one if the definitions of p_{rot} and p_ψ themselves depended on the q^1 to q^{n-6} or on the $\dot{q}^1$ to $\dot{q}^{n-6}$. They do not so depend, it can be shown, since the vibrational angular momenta were neglected.

The argument leading to Eq. (23) is again applicable, provided the integration in (24) is first performed at fixed p_{rot} and p_ψ, reserving for the last two integrations those over p_{rot} and p_ψ. The $g^{ij\ddagger}$ appearing in $T^\ddagger$ (Eq.28) are again conjugate to the g_{ij} on an n-1 dimensional subspace. Indeed, because of the neglect of certain g_{ij}'s and g^{ij}'s the $g^{ij\ddagger}$ are conjugate to the g_{ij} on the subspace of coordinates of the activated complex for which the orientation of the complex is fixed ($d\theta = d\phi = d\psi = 0$). (Because of the vanishing of certain other g_{ij}'s and g^{ij}'s the $g^{ij\ddagger}$ are even conjugate to the g_{ij} on the internal coordinate subspace of the complex.)

Restriction of an operation to an n-3 dimensional subspace in which the orientation of the complex is fixed (i.e. $d\theta=d\phi=d\psi=0$) will be designated by a bar, e.g. in $\overline{\sum_i}$, $\overline{\det_{i,j}}$, $\overline{\det_{i,j\neq r}}$ and $\overline{\prod_{i\neq r}}$. In all cases i = 1 to n-3 and, where indicated, $i \neq r$.

Integration over all momenta but p_θ, p_ϕ and p_ψ in (24) and over all momenta in (25) may be performed. By arguments similar to those given previously one obtains (32) and (44).

$$e^{-F^\ddagger/kT} = (2\pi kT)^{\frac{n-4}{2}} \int \left[\int e^{-U^\ddagger/kT} \, d\bar{\sigma}/h^{n-1} \right] e^{-T_{rot}/kT} \, d\tau_{rot} \,, \qquad (44)$$

where

$$d\bar{\sigma} = \left(\overline{\det_{i,j\neq r}} \, g_{ij}\right)^{\frac{1}{2}} \overline{\prod_{i\neq r}} \, dq^i \qquad (45)$$

and

$$d\tau_{rot} = \prod_\alpha dq^\alpha \, dp_\alpha \,, \qquad (46)$$

with $\alpha = \theta$, ϕ and ψ. The integrand in the integral over $\prod_{i \neq r} dq^i$ in (44) depends on the angular momenta but only via p_{rot} and p_ψ. If p_x, p_y and p_z are the components of p_{rot} along the body-fixed principal axes, the symmetry axis being the z-axis and p_z thereby being equal to p_ψ, then $dp_\theta\, dp_\phi\, dp_\psi$ equals $\sin\theta\, dp_x\, dp_y\, dp_\psi$ and p^2_{rot} equals $p_x^2 + p_y^2 + p_\psi^2$. Eq. (43) may be integrated in part,[21] yielding (47) where the limits on p_ψ are $-p_{rot}$ to $+p_{rot}$.

$$e^{-F^\ddagger/kT} = (2\pi kT)^{\frac{n-1}{2}} \int \left(\int e^{-U^\ddagger/kT}\, d\bar{\sigma}/h^{n-1} \right) e^{-T_{rot}/kT} \quad (47)$$

$$\pi \sin\theta \prod_\alpha dq^\alpha\, dp_\psi\, dp^2_{rot}$$

The masses can be extracted from (47):

The quantity conjugate to g_{rr} on the n-3 dimensional subspace, denoted by $\bar{g}^{rr}$, equals $\overline{\det}_{i,j \neq r}\, g_{ij}/\bar{g}$, where $\bar{g}$ is $\overline{\det}\, g_{ij}$. However, since the determinant of the g_{ij}'s of the three rotations equals $A^2C\sin^2\theta$ and since certain g_{ij} cross-terms were neglected, $\bar{g}$ equals $g/A^2C\sin^2\theta$. From g one may now extract $\prod_{i=1}^{n} m^i$, as in (11).

A reduced mass $\bar{m}^\ddagger$ for motion normal to S can again be defined, but now only on the n-3 dimensional subspace. Otherwise an inconsistency would occur. If the quantity conjugate to a_{ij} on this subpace is denoted by $\bar{a}^{ij}$ then the argument which led to (34) leads to (48), when applied to this subspace.

$$\bar{m}^{\ddagger} = \bar{a}^{rr}/\bar{g}^{rr} \tag{48}$$

The area element dS of the hypersurface of constant q^r in n-dimensional space, for any given p_{rot} and p_ψ, is $(aa^{rr})^{\frac{1}{2}} \prod_{i\neq r} dq^i$. It also equals $d\bar{\sigma} \sin\theta \, (\prod_a dq^a)$. On introducing these results one finds:

$$e^{-F^{\ddagger}/kT} = \frac{(2\pi kT)^{\frac{n-4}{2}}}{h^{n-1}} \prod_{i=1}^{n} (m^i)^{\frac{1}{2}} \int\int\left[\int \frac{e^{-U^{\ddagger}/kT} \, dS}{(A^2C\,\bar{m}^{\ddagger}\, a^{rr}/\bar{a}^{rr})^{\frac{1}{2}}}\right] e^{-T_{rot}/kT} \pi \, dp_\psi dp^2_{rot} \tag{49}$$

On introducing Eq. (35) for dS and performing several integrations one obtains (50).

$$e^{-F^{\ddagger}/kT} = (2\pi\, kT/h^2)^{\frac{n-1}{2}} \; 4\pi \prod_{i=1}^{n} (m^i)^{\frac{1}{2}} \int\int\left[\int \frac{R^2 e^{-U^{\ddagger}/kT} \, dS_{int}}{(\bar{m}^{\ddagger}\, a^{rr}/\bar{a}^{rr})^{\frac{1}{2}}}\right] \frac{e^{-T_{rot}/kT}}{(A^2C)^{\frac{1}{2}}} du_\psi \, du_{rot} \tag{50}$$

where

$$u_{rot} = p^2_{rot}/2kT$$

$$u_\psi = p_\psi/(2\pi kT)^{\frac{1}{2}}$$

(When the integral over S_{int} is independent of p_{rot} and p_ψ one may interchange the order of integration of dS_{int} and $du_\psi \, du_{rot}$. One then finds that $\int \exp(-T_{rot}/kT \, du_\psi \, du_{rot} \, (A^2C)^{-\frac{1}{2}}$ equals unity, since p_ψ is integrated from $-p_{rot}$ to $+ p_{rot}$ and p_{rot} is integrated from 0 to ∞.)

The relation of $\bar{a}^{rr}$ to a^{rr}, can be deduced from determinant theory, and the results are given in Appendix III. Conditions under which a^{rr} and $\bar{a}^{rr}$ are equal are also described there, namely when the cross terms a^{ri} vanish if i is a rotation.

From (23), (32) and (50) one obtains:

$$(\text{bimolecular})\ k_{rate} = (8\pi kT)^{\frac{1}{2}} \int \left[\int \frac{R^2 e^{-U^{\ddagger}/kT}}{(m^{\ddagger}\ a^{rr}/\bar{a}^{rr})^{\frac{1}{2}}} dS_{int} \right] \frac{e^{-T_{rot}/kT} du_{\psi} du_{rot}}{(A^2 C)^{\frac{1}{2}} Q} \qquad (51)$$

where Q is a configurational integral for the reactants, defined by (40).

$$(\text{unimolecular})\ k_{rate} = (kT/2\pi)^{\frac{1}{2}} \int \left[\int \frac{e^{-U^{\ddagger}/kT}\, dS_{int}}{(m^{\ddagger}\ a^{rr}/\bar{a}^{rr})^{\frac{1}{2}}} \right] \frac{e^{-T_{rot}/kT} du_{\psi} du_{rot}}{(A^2 C)^{\frac{1}{2}} Q} \qquad (52)$$

The "diatomic" approximation is readily derived from (51) or (52). Inspection of the derivation reveals that these equations apply, with $du_{\psi}\,(C)^{-\frac{1}{2}}$ omitted, with T_{rot} equal to $p_{rot}^2/2A$, with $p_{rot}^2 = p_x^2 + p_y^2$, and with the bar on $\bar{a}^{rr}$ and $\bar{g}^{rr}$ indicating that they are conjugate to a_{rr} and g_{rr} on an n-2 dimensional subspace. One obtains:

$$(\text{bimolecular})k_{rate} = (8\pi kT)^{\frac{1}{2}} \int \left[\int R^2 e^{-U^{\ddagger}/kT} (A^2 m^{\ddagger} a^{rr}/\bar{a}^{rr})^{-\frac{1}{2}}\ dS_{int} \right] e^{-T_{rot}/kT} du_{rot}/Q \qquad (53)$$

$$(\text{unimolecular})k_{rate} = (kT/2\pi)^{\frac{1}{2}} \int \left[\int e^{-U^{\ddagger}/kT} (A^2 m^{\ddagger} a^{rr}/\bar{a}^{rr})^{-\frac{1}{2}}\ dS_{int} \right] e^{-T_{rot}/kT} du_{rot}/Q \qquad (54)$$

A special case of this diatomic approximation in which the coordinate q^r was taken to be R, the separation distance of the reactants in the ion-molecule system[17] or in the recombining radical system[16], can be derived from (53) as follows:

In the rotation plus reaction coordinate subspace the line element is

$$ds^2 = dR^2 + R^2\sin^2\theta\, d\phi^2 + R^2 d\theta^2,$$

from which the corresponding a_{ij}'s are given immediately. In this orthogonal coordinate system the a^{ij}'s also vanish for $i \neq j$. It the follows from Appendix II (A9) that $\bar{a}^{rr}$ equals a^{rr}. Again, in this system one easily verifies that $m^{\ddagger}$ equals μ, the reduced mass of the two reactants. The approximation was also made[16,17] that $U^{\ddagger}$ is the sum of a term depending solely on R, U(R), and of the potential energy of the internal coordinates, where R is now the value of R which maximizes the integrand at the given p_{rot}. Thereby, one obtains:

$$k_{rate} = (8\pi kT)^{\frac{1}{2}} \int R^2\, e^{-U(R)/kT}\, \mu^{\frac{1}{2}}\, e^{-p_{rot}^2/2\mu R^2 kT}\, dp_{rot}^2/2\mu R^2 kT \qquad (55)$$

where R is a function of p_{rot}, being the solution of

$$\frac{\partial U}{\partial R} - \frac{p_{rot}^2}{\mu R^3} = 0 \qquad (56)$$

Geodesic Normal Coordinates

For any reaction hypersurface S a coordinate system may be defined for which g_{ri} vanishes for $i \neq r$ and for which g_{rr} is a constant:[22] A coordinate system $q^i (i=1 \text{ to } n, i \neq r)$ is first defined on the surface in mass-weighted space. The coordinates of any point off this surface are then defined by drawing the geodesic through the point, such that the geodesic cuts the hypersurface orthogonally. The q^i for $i \neq r$ are then assigned the same values as those occurring at the intersection of the geodesic and the hypersurface. The value for q^r is set equal to the arc length along this geodesic from the hypersurface to the point. Hence, $ds^2 = g_{rr}(dq^r)^2 = (dq^r)^2$ along this geodesic in mass-weighted space. The line element in this space is:

$$ds^2 = \sum_{i,j \neq r} g_{ij}\, dq^i dq^j + (dq^r)^2 \tag{57}$$

Correspondingly, it can be shown, g^{ri} vanishes for $i \neq r$, and g^{rr} equals unity. The kinetic energy then has the following simple form.

$$T = \tfrac{1}{2} \sum_{i,j \neq r} g^{ij}\, p_i\, p_j + \frac{p_r^{\,2}}{2} \tag{58}$$

(p_i equals $\partial[(ds/dt)^2/2] / \partial \dot{q}^i$). If the definition of q^r is modified so that ds^2 equals $\mu\, (dq^r)^2$ along the geodesic, where μ is some constant then the coefficient of p_r^2 would be $1/2\,\mu$ instead.

After having made a choice of geodesic normal coordinates one may use (58) and derive the activated complex theory rate equation in the usual way, obtaining an expression analogous to (23). Upon introducing a canonical coordinate transformation to any other coordinates q^i and to their conjugate momenta, p_i, such as those occurring in (24), Eq. (23) is obtained because of the invariance of the Hamiltonian and of the phase space volume element to such canonical transformations.

It is clear, therefore, why (23) is the same as the usual activated complex rate equation in the literature.

It is of interest to compare further the above derivation of (23) with the usual one in the literature. In that case assumptions 4 is made, though we have seen that if one introduces geodesic normal coordinates no assumption is made in using a kinetic energy expression of the form (58). Even without the introduction of these coordinates, (58) can be used if a fifth assumption, often made in activated complex theory, is added. The potential energy is expanded about a saddle-point (when it occurs) and only the quadratic powers of the displacements are retained; normal coordinates are then introduced and rotation-vibration interaction is neglected. In this case g^{ri} is in fact zero and the kinetic energy is of the form (58). However, when the reaction occurs in solution and many solvent molecules participate in the complex, the retention of only quadratic terms is presumably not valid for the many-coupled rotations of these solvent molecules, though it presumably is valid for vibrations.

One advantage of the derivation of Eq. (23) given in the earlier section as compared with one based on geodesic normal coordinates is that a more direct comparison with the step-by-step derivation of the quantum form of (23) is possible in the former case. We have seen elsewhere[4] that certain coordinate systems are more useful than others in the quantum derivation: they permit one to make a local approximation of the potential energy surface in the vicinity of a saddle-point by one which permits separation of variables. Such coordinate systems do not involve geodesic normal coordinates, except in a special case.

Appendix I. Invariance of $m^{\ddagger}$, a^{rr} and g^{rr} to Changes in External Coordinates

For notational convenience, the Cartesian coordinates $x^1, \ldots, x^n$ of the atoms in the activated complex will be written in this appendix as $x^1, y^1, z^1, \ldots, x^{\frac{n}{3}}, y^{\frac{n}{3}}, z^{\frac{n}{3}}$. When the Cartesian coordinates are varied at any fixed values of the internal coordinates the value of q^r is unchanged. If the $x^1, \ldots, z^{\frac{n}{3}}$ are so transformed to new values, $\bar{x}^1, \ldots \bar{z}^{\frac{n}{3}}$ by variation of one or more external coordinates we have, therefore:

$$q^r(x^1, \ldots, z^{\frac{n}{3}}) = q^r(\bar{x}^1, \ldots, \bar{z}^{\frac{n}{3}}) \qquad (A1)$$

Any new set $\bar{x}^i, \bar{y}^i, \bar{z}^i$ is a function only of x^i, y^i, z^i: If $\bar{\underset{\sim}{r}}^i$ and $\underset{\sim}{r}^i$ are column vectors with elements $\bar{x}^i, \bar{y}^i, \bar{z}^i$ and x^i, y^i, z^i, respectively. They are related according to (A2).

$$\bar{\underset{\sim}{r}}^i = \underset{\sim}{R} + \underset{\sim}{A}\,\underset{\sim}{r}^i \qquad (A2)$$

where $\underset{\sim}{R}$ is a column vector whose elements are the x, y and z components of the translational displacement and $\underset{\sim}{A}$ is an orthogonal matrix describing the rotation.

By differentiation of (A1) Eq. (A3) is obtained.

$$\frac{\partial^2 q^r}{\partial \bar{x}^{i\,2}} + \frac{\partial^2 q^r}{\partial \bar{y}^{i\,2}} + \frac{\partial^2 q^r}{\partial \bar{z}^{i\,2}} = \sum_{\alpha=x,y,z} \left(\frac{\partial^2 q^r}{\partial x^{i\,2}} l_{x\alpha}^2 + \frac{\partial^2 q^r}{\partial y^{i\,2}} l_{y\alpha}^2 + \frac{\partial^2 q^r}{\partial z^{i\,2}} l_{z\alpha}^2 + 2\frac{\partial^2 q^r}{\partial x^i \partial y^i} l_{x\alpha} l_{y\alpha} + 2\frac{\partial^2 q^r}{\partial x^i \partial z^i} l_{x\alpha} l_{z\alpha} + 2\frac{\partial^2 q^r}{\partial y^i \partial z^i} l_{y\alpha} l_{z\alpha} \right) \qquad (A3)$$

where the l's are the elements of the matrix $\underset{\sim}{A}$. Because of the orthogonal nature of this matrix it follows that the right hand side of (A3) equals

$$\frac{\partial^2 q^r}{\partial x^{i^2}} + \frac{\partial^2 q^r}{\partial y^{i^2}} + \frac{\partial^2 q^r}{\partial z^{i^2}} \quad . \tag{A4}$$

This invariance of $\nabla_i{}^2 q^r$ holds for all i (1 to n). Recalling the definition of g^{rr} and a^{rr} in Eqs. (3) and (9), it follows that they are also invariant to changes in the values of the external coordinates.

Appendix II. Factoring of dS.

On recalling the value of dS in Eq. (19) and the fact that a^{rr} was shown in Appendix I to depend on the internal coordinates alone, it suffices to show that $\underline{a}$ can be factored in order to show that dS can be factored into two terms, one depending on the internal coordinates, the other depending on the external coordinates. Inasmuch as the volume element dV equals $a^{\frac{1}{2}} \prod_{i=1}^{n} dq^i$ and it has been shown that it can be so factored, for example by a serial method,[23] $\underline{a}$ can be factored and the proof is complete. To show that the final result of the factoring is of the form (35) to (37) we may proceed as follows:

In the serial method one puts one atom of the activated complex any place in the system, specifying its coordinates as x, y, and z. Another atom is then characterized by coordinates relative to the first (e.g.,polar coordinates R, θ, ϕ). A third atom is then characterized by coordinates relative to the first two, and so on. The volume element is found to be a product $\prod_{i=1}^{n} V_i$, of which V_i depends on the i'th set of (relative) coordinates alone.[23] For example, V_1 is dxdydz, V_2 is $R^2 \sin\theta \, d\theta \, d\phi \, dR$, etc. Hence:

$$a^{\frac{1}{2}} \prod_{i=1}^{n} dq^i = dV = dxdydz \sin\theta \, d\theta d\phi dR \, (R^2 \, dr \prod_{i=3}^{n} dV_i) \qquad (A5)$$

One may now transform the coordinates on the r.h.s. of (A5) to the coordinates used in the body of this paper $(q^1,\ldots q^n)$ such that five of the q^i's are x, y, z, θ and ϕ, the remaining ones being the "internal coordinates" of the activated complex. It follows from (A5) that $a^{\frac{1}{2}}$ equals $dxdydz \sin\theta \, d\theta \, d\phi$ multiplied by a function of the internal coordinates alone, a function which contains factor R^2, exhibited in (35). In the case of heterogeneous reactions only x and y are the "external coordinates" and Eq. (37) follows.

Some reactions in solution, pure electron transfer reactions, involve no bond ruptures and it is useful to factor dV in a slightly different form: Let the coordinates of one reactant be transformed to the translations of its center of mass, to the rotations about this center and to the vibrations. Let the coordinates of the other reactant be transformed to its own translations, rotations and vibrations. Then from the six translations six new coordinates can be introduced: the three translations (x, y, z) of the center of these two masses, the orientation of the line of centers (θ, ϕ) and the separation distance of the two centers (R). The coordinates of all the molecules in the medium can be transformed to relative coordinates with respect to this line of centers (and separation distance). The element dV once again has the form (A5), but with the above interpretation of x, y, z, θ, ϕ, R, and dS has the form (35). In computing dS_{int}, one center of mass is to be held fixed and the other constrained to move along a fixed line, because of this factoring.

Appendix III. Relation of $\bar{a}^{rr}$ to a^{rr}.

We shall use the following theorem:[24] If M is a minor in the determinant of the a^{ij}'s, if m is the corresponding minor in the determinant of a_{ij}'s, and if $\tilde{m}$ is the algebraic complement of m in $\underline{a}$ then:

$$M = \tilde{m}\, a^{-1} \tag{A6}$$

The minor in $\underline{a}$ formed by the a_{ij}'s from the rotational coordinates and from q^r will be denoted by a_{rx} while that formed by the a^{ij}'s for these coordinate in det a^{ij} will be denoted by $a^{r\chi}$. From (A6) one finds:

$$a^{r\chi} = \tilde{a}_{r\chi} \quad a^{-1} = \bar{a}\,\bar{a}^{rr} \quad a^{-1} \tag{A7}$$

since $\bar{a}\,\bar{a}^{rr}$ is the algebraic complement of a_{rr} in $\bar{a}$ and, inspection shows, so is $\tilde{a}_{r\chi}$. However, when M in (A6) is taken to be the minor formed by the a^{ij}'s of the rotational coordinates alone, it will be called a^{χ}. Then, $\tilde{m}$ is simply $\bar{a}$. From (A6) one then finds

$$a^{\chi} = \bar{a}\, a^{-1} \tag{A8}$$

From (A7) and (A8) one obtains, finally,

$$\bar{a}^{rr} = a^{r\chi}(a^{\chi})^{-1} \tag{A9}$$

Inasmuch as $a^{r\chi}$ and a^{χ} are minors with a^{ij}'s as elements, and the former contains a^{rr}, a relation between $\bar{a}^{rr}$ and a^{rr} has been obtained.

When the cross-terms a^{ri} for i equal to a rotational coordinate equal zero, $a^{r\chi}$ factors into $a^{rr}\, a^{\chi}$. One then has:

$$\bar{a}^{rr} = a^{rr} \tag{A10}$$

These a^{ri}'s vanish when the coordinate hypersurfaces of the rotations are each orthogonal to the q^r-coordinate hypersurface. The example cited in the text is a special case of this situation in which all coordinate hypersurfaces for the coordinates are mutually orthogonal.

References

1. E.g., H. Eyring, J. Chem. Phys. 3, 107 (1935); H. Eyring, J. Walter and G. Kimball, Quantum Chemistry, John Wiley and Sons, New York, 1944, Chapter 16; E. Wigner, Trans. Faraday Soc. 34,29 (1938) and Z. physik. Chem. B19, 203 (1932); G. H. Vineyard, J. Phys. Chem. Solids 3, 121 (1957).
2. Normally, the potential energy is expanded about a saddle-point, retaining only quadratic terms, a normal coordinate analysis is made, and rotation-vibration interaction is neglected. The reaction hypersurface then becomes a hyperplane, the reaction coordinate thereby becomes Cartesian, and assumption 4 is then valid.
3. L. Landau, Physik. Z. Sowjetunion 2, 46 (1932); C. Zener, Proc. Roy. Soc. (London) A137 696 (1932); C. A. Coulson and K. Zalewski, Proc. Roy. Soc. (London) A268, 437 (1962).
4. R. A. Marcus, J. Chem. Phys. (in press).
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7. See, for example, C.E.Weatherburn, Riemannian Geometry, Cambridge University Press (1957), p. 24.
8. See, for example, P. Stäckel, Habilitationschrift, Halle, Germany (1891); Decius, Wilson and Cross, Ref. 18, p. 279; or, in the case of n=3, H. C. Corben and P. Stehle, Classical Mechanics, (John Wiley and Sons, New York, 1950), p.12, where x^i is our $(m^i)^{\frac{1}{2}} x^i$.
9. Following a standard convention we use i superscripts on $\dot{q}^i$ and i subscripts on p_i, since the former are components of a contravariant vector and the latter are components of a covariant vector (cf. Ref.7, p.22).

10. On multiplying (6) by g^{ik}, summing over k, and using (4) one finds that $q^i = \sum_{j=1}^{n} g^{ij} p_j$. Introduction into (5) yields (7).

11. For example, if $\underset{\sim}{g}$ denotes a square matrix whose components are g_{ij}, and $\underset{\sim}{m}$ denotes a diagonal matrix whose diagonal components are m^k, and $\underset{\sim}{c}$ a square matrix whose components are $\partial x_i / \partial q_j$, then Eq. (2) can be written as $\underset{\sim}{g} = \underset{\sim}{\tilde{c}}\ \underset{\sim}{m}\ \underset{\sim}{c}$ where $\underset{\sim}{\tilde{c}}$ is the transpose of $\underset{\sim}{c}$. On taking the determinant of both sides and applying the product rule Eq. (11) immediately follows.

12. Ref. 7, p. 42.

13. See, for example, ref. 5, Appendix III.

14. In any submicroscopic region of the interface we shall draw a plane near the interface (exactly parallel when the surface is uniform), such that the distance from the interface to the plane varies from point to point only because of surface roughness. The Cartesian coordinates in the plane and in any parallel plane are x and y.

15. R. A. Marcus, J. Chem. Phys. 41, 000 (1964), Footnote 14.

16. E. Gorin, Acta Physicochim. U.R.S.S. 9, 691 (1938); E. Gorin, W. Kauzmann, J. Walter and H. Eyring, J. Chem. Phys. 7, 633 (1939).

17. H. Eyring, J. O. Hirschfelder and H. S. Taylor, J. Chem. Phys. 4, 479 (1936). G. Gioumousis and D. P. Stevenson, ibid 29, 294 (1958) made assumptions equivalent to those of these authors but calculated reaction cross-sections instead.

18. E. B. Wilson, Jr., J.C. Decius and P. C. Cross, Molecular Vibrations (McGraw-Hill Book Company, Inc. 1955) p. 284, where we use the actual moments of inertia instead of the equilibrium ones and where the expression can be shown to be of the form of the present Eq.(41)

(using their notation)
by adding and subtracting $M_z^2/2I_z^o$ and noting that p_{rot}^2 equals $M_x^2 + M_y^2 + M_z^2$ there.

19. C. Eckart, Phys. Rev. 47, 552 (1935); Cf Wilson, Decius and Cross, Ref. 18, Chap. 11 and reference cited therein.

20. This Jacobian can be found from the expressions for p_θ, p_ϕ and p_χ in terms of p_x, p_y and p_z in Ref. 18, p. 282, Eq. 6, where M_x is p_x, etc.

21. The p_x, p_y, p_z are transformed to new coordinates p_{rot}, α and p_z, where α is a polar angle in any plane parallel to the p_x, p_y plane in p_x, p_y, p_x space: $p_x = r \cos \alpha$, $p_y = r \sin \alpha$, $p_z = p_z$, with $r^2 = p_{rot}^2 - p_z^2$. The Jacobian of this transformation equals p_{rot}. Since the integrand in (43) depends on p_{rot} and p_z but not on α, integration over α may be performed, yielding a factor of 2π.

22. J. L. Synge and A. Schild, Tensor Calculus (University of Toronto Press, Toronto, Canada, 1949), p. 71.

23. D. R. Hershbach, H. S. Johnston and D. Rapp, J. Chem. Phys. 31, 1652 (1959).

24. M. Bocher, Introduction to Higher Algebra (The Macmillan Company, New York 1907), p. 31. One uses the fact that the elements of the adjoint of a are aa^{ij}.