

synthesized, stereospecifically labeled metal carbonyl substitution products of the types *cis*-(L)¹³CO-M(CO)₄^{45,46} and *cis*-(L₂)(¹³CO)M(CO)₃⁴⁶ can afford unequivocal information about the sites of reactivity through studies of the degree of label retention during the course of their ligand-exchange reactions. The development and perfection of matrix-isolation techniques which involve cocondensation of a metal carbonyl and an inert gas matrix material such as Ar have facilitated the study of species formed upon uv irradiation. Many such species may resemble highly reactive intermediates formed through thermal reactions.²⁷ It is anticipated that theoretical calculations for such intermediates⁴⁷ will augment experimental observations of their relative stabilities, their geometries, and the orientations of their substituents. Such studies should provide useful insight into the nature of reaction intermediates and paths of reaction.

(45) C. L. Hyde and D. J. Darensbourg, *Inorg. Chem.*, **12**, 1286 (1973).

(46) M. A. Cohen and T. L. Brown, *Inorg. Chem.*, **15**, 1417 (1976); D. J. Darensbourg and G. R. Dobson, unpublished results.

(47) A recent paper has described molecular orbital calculations for penta-coordinate metal carbonyls of square-pyramidal and trigonal-bipyramidal geometries: A. R. Rossi and R. Hoffmann, *Inorg. Chem.*, **14**, 365 (1975).

Other developments of a theoretical nature, particularly, molecular orbital calculations of increasing sophistication for series of derivatives, are expected to be tested employing reactivity data and physical data such as ir and uv-visible spectra. The increasing availability of ¹³C NMR instrumentation is affording a growing body of data which may eventually prove to be of use in this regard.⁴⁸

Future studies of these and other kinds should ultimately lead to detailed understanding of ligand-exchange processes in octahedral metal carbonyls.

It is a pleasure to acknowledge the contributions to this research area of my past and present students and postdoctoral fellows, whose names are to be found among the references. The financial support of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation, the Robert A. Welch Foundation, and the North Texas State University Faculty Research Fund is gratefully acknowledged. Professors D. J. Darensbourg, M. Y. Darensbourg, and T. L. Brown have made helpful comments regarding this presentation.

(48) For a recent review, see L. J. Todd and J. R. Wilkinson, *J. Organometal. Chem.*, **77**, 1 (1974).

Importance of Nonseparability in Quantum Mechanical Transition-State Theory

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The transition-state theory¹ of chemical kinetics has without doubt provided the most useful phenomenological framework for parameterizing rate constants for a wide variety of chemical reactions. Recently,²⁻⁷ however, there has been interest in investigating the dynamical basis of transition-state theory and trying to learn the extent to which it provides a *quantitative* description of rate constants for elementary bimolecular reactions.

One of the practical motivations for this recent direction of research is the recognition that, for chemical reactions with significant activation energy, transition-state theory describes the *threshold* region of the reactive cross section quite well, and this⁸ is the energy regime most important for determining the thermal rate constant. Since the threshold region is often described rather poorly by classical trajectory methods⁹—which

are useful for describing many other aspects of the dynamics of simple chemical reactions—transition-state theory is an important complement to trajectory methods. (It is interesting that an analogous complementarity also exists experimentally: the “modern” methods of chemical kinetics—e.g., crossed molecular beams, infrared chemiluminescence, various laser techniques, etc.—provide dynamical information about reactions which have little or no activation energy (or at energies significantly above any threshold), but it is difficult to extract information about the threshold

(1) The development of transition-state theory is associated with the names of Wigner, Pelzer, Polanyi, Evans, and particularly Eyring; see, for example, the brief historical discussion and bibliography in K. J. Laidler, “Theories of Chemical Kinetics”, McGraw-Hill, New York, N.Y., 1969, pp 41–43. The classic textbook reference to traditional transition-state theory is S. Gladstone, K. J. Laidler, and H. Eyring, “Theory of Rate Processes”, McGraw-Hill, New York, N.Y., 1941.

(2) R. A. Marcus, *J. Chem. Phys.*, **45**, 2138, 2630 (1966); **46**, 959 (1967).

(3) J. C. Keck, *Adv. Chem. Phys.*, **13**, 85 (1967); *Adv. At. Mol. Phys.*, **8**, 39 (1972).

(4) K. Morokuma and M. Karplus, *J. Chem. Phys.*, **55**, 63 (1971).

(5) G. W. Koeppel and M. Karplus, *J. Chem. Phys.*, **55**, 4667 (1971).

(6) (a) P. Pechukas and F. J. McLafferty, *J. Chem. Phys.*, **58**, 1622 (1973); (b) *Chem. Phys. Lett.*, **27**, 511 (1974).

(7) W. H. Miller, *J. Chem. Phys.*, **61**, 1823 (1974).

(8) See, for example, R. Wolfgang, *Acc. Chem. Res.*, **2**, 248 (1969).

(9) For recent reviews, see D. L. Bunker, *Methods Comput. Phys.*, **10**, 287 (1971), and R. N. Porter, *Annu. Rev. Phys. Chem.*, **25**, 317 (1974).

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behavior of the reactive cross section from such measurements. More traditional kinetics methodology—i.e., determination of the rate constant as a function of temperature—on the other hand provides a sensitive measure of the threshold region (but essentially only this.)

Although it is apparent from the physical assumptions inherent in transition-state theory (vide infra) that it *should* describe the threshold region accurately, the most detailed comparisons¹⁰ of conventional transition-state theory with “exact” results from quantum scattering calculations have shown it to be poor at moderate and low temperatures. This disappointing result seems to be a consequence of the fact that an assumption of *separability* of motion along a reaction coordinate is inextricably bound up in the usual quantum mechanical version of transition-state theory, and separability has been seen in a variety of calculations to be a poor approximation in the threshold region. If transition-state theory is to provide a quantitative description of the reactive cross section in the threshold region (and thus the rate constant), it must therefore be applied quantum mechanically, because quantum effects are important at threshold, but without assuming the reaction dynamics to be separable.

The weakness of the separability approximation in conventional transition-state theory was recognized quite clearly by Johnston and Rapp¹¹ a number of years ago, and they proposed ways of trying to overcome it. While not rigorous or accurate quantitatively, these early attempts at dealing with nonseparability in transition state theory were important in identifying this feature as a crucial weakness.

This Account first reviews the dynamical basis of transition-state theory within the framework of *classical* mechanics, emphasizing the “fundamental assumption” on which it is based. Examples are presented showing that in a classical world transition-state theory is an excellent approximation in the threshold region. It is then shown how a quantum mechanical version of transition-state theory can be constructed which escapes the necessity of assuming separability. Results of calculations based on this theory are seen to be in good agreement with (exact) quantum mechanical scattering theory.

Classical Transition-State Theory and the Fundamental Assumption

As Wigner¹² emphasizes, transition-state theory is a model essentially based on classical mechanics. (The validity of classical mechanics to describe the nuclear dynamics is Wigner's¹² second assumption; his first assumption is use of the Born–Oppenheimer approximation to separate electronic and nuclear motion and the assumption that only one potential-energy surface is involved in the reaction.) To gain a feeling for the dynamical approximations inherent in transition-state theory it is therefore useful first to discuss classical transition-state theory before considering a quantum mechanical version of it.

If the reactants are in a Boltzmann distribution of their internal states and relative translation, then the

classical rate constant is a Boltzmann average of the flux of reactive trajectories through a surface which divides reactants from products. More precisely, the expression for the exact rate constant in classical mechanics is¹³

$$k_{b \leftarrow a}(T) = Q_a^{-1} h^{-F} \int d\mathbf{p} \int d\mathbf{q} e^{-\beta H(\mathbf{p}, \mathbf{q})} \delta[f(\mathbf{q})] \times \frac{\partial f(\mathbf{q})}{\partial \mathbf{q}} \cdot \mathbf{p} / m \chi_{b \leftarrow a}(\mathbf{p}, \mathbf{q}) \quad (1)$$

where $\beta = (kT)^{-1}$, $(\mathbf{p}, \mathbf{q}) = (p_i, q_i)$, $i = 1, \dots, F$ are the momenta and coordinates of the system with F degrees of freedom, Q_a is the partition function per unit volume of the noninteracting reactants, $H(\mathbf{p}, \mathbf{q})$ is the total Hamiltonian for the system, and $f(\mathbf{q})$ is a function of the coordinates which defines the *dividing surface* via eq 2

$$f(\mathbf{q}) = 0 \quad (2)$$

δ is the Dirac delta function (the factor $\delta(f(\mathbf{q}))$ in eq 1 converts the “volume” integral over all F coordinates into a “surface” integral over $F - 1$ coordinates), and $\chi_{b \leftarrow a}(\mathbf{p}, \mathbf{q})$ is the *characteristic function* for reaction. The definition of $\chi_{b \leftarrow a}(\mathbf{p}, \mathbf{q})$ is that

$$\chi_{b \leftarrow a}(\mathbf{p}, \mathbf{q}) = 1 \quad (3)$$

if the trajectory determined by the phase point (\mathbf{p}, \mathbf{q}) is reactive in the $a (A + BC) \rightarrow b (AB + C)$ direction, and is zero otherwise.

It is illustrative to write out eq 1 more explicitly for the simplest possible example, a collinear $A + BC \rightarrow AB + C$ reaction. $F = 2$ in this case, and the two coordinates can be chosen to be r and R , which denote the relative B–C vibrational coordinate and the distance from A to the center of mass of BC, respectively; p and P are the momenta conjugate to r and R . The function $f(r, R)$ which corresponds to choosing the dividing surface far out in the reactant region—surface S_1 in Figure 1—is

$$f(r, R) = R_{\max} - R \quad (4)$$

It is then not hard to see that eq 1 becomes

$$k_{b \leftarrow a} = Q_a^{-1} h^{-2} \int_{-\infty}^{\infty} dr \int_{-\infty}^{\infty} dp \int_{-\infty}^{\infty} dP \times \left(-\frac{P}{\mu} \right) e^{-\beta H(P, R, p, r)} \chi_{b \leftarrow a}(P, R, p, r) \quad (5)$$

with $R = R_{\max}$ and where μ is the reduced mass for the A–BC translational motion. If R_{\max} is sufficiently large, the Hamiltonian is given by its asymptotic form

$$\lim_{R \rightarrow \infty} H(P, R, p, r) = \frac{P^2}{2\mu} + h(p, r)$$

where $h(p, r)$ is the vibrational Hamiltonian for the isolated BC molecule; also, it is clear that trajectories beginning on this surface with $P > 0$ cannot be reactive in the $a \rightarrow b$ direction. Thus if the translational energy E_t is introduced,

$$E_t = \frac{P^2}{2\mu}$$

eq 5 takes on its more conventional form

$$k_{b \leftarrow a} = Q_a^{-1} \left(\frac{kT}{h} \right) h^{-1} \int_{-\infty}^{\infty} dr \int_{-\infty}^{\infty} dp \int_0^{\infty} d(\beta E_t) \times e^{-\beta E_t} e^{-\beta h(p, r)} \chi_{b \leftarrow a}(P, R, p, r) \quad (6)$$

(13) See, for example, ref 3 and 6a.

(10) D. G. Truhlar and A. Kuppermann, *Chem. Phys. Lett.*, **9**, 269 (1971); *J. Chem. Phys.*, **36**, 2232 (1972).

(11) H. S. Johnston and D. Rapp, *J. Am. Chem. Soc.*, **83**, 1 (1961).

(12) E. Wigner, *Trans. Faraday Soc.*, **34**, 29 (1938).

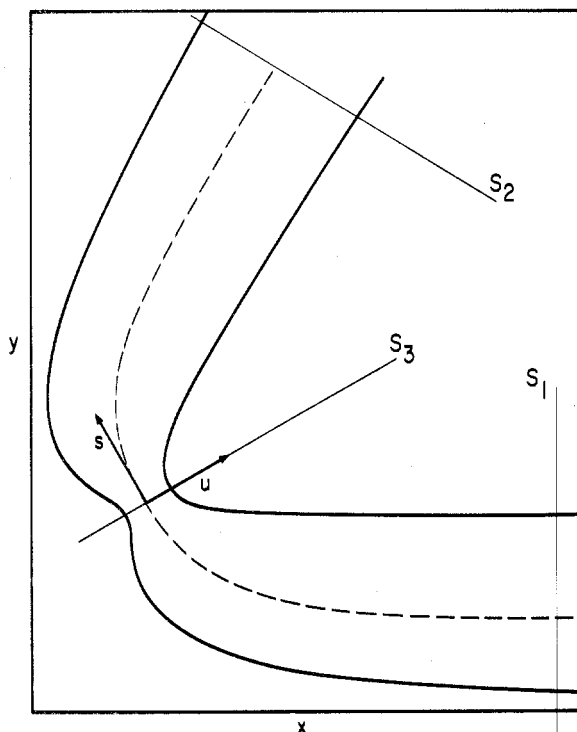


Figure 1. Sketch of a collinear potential energy surface for a symmetric $A + BC \rightarrow AB + C$ reaction (i.e., $A \equiv C$). x and y are mass weighted, or "skewed" coordinates that diagonalize the kinetic energy: $x = R(\mu/M)^{1/2}$, $y = r(m/M)^{1/2}$, where R and r are the translational and vibrational coordinates, respectively, and μ and m the corresponding reduced masses [$m = BC/(B + C)$, $\mu = A(B + C)/(A + B + C)$], M is any arbitrary mass, and the classical kinetic energy is $\frac{1}{2}M(x^2 + y^2)$. s and u are the linear combinations of x and y which diagonalize the potential energy at the saddle point. S_1 , S_2 , and S_3 indicate the "surfaces" which are referred to in the text.

with $R = R_{\max}$ and $P = -(2\mu E_t)^{1/2}$. Equation 6 is the standard expression for which a Monte-Carlo trajectory calculation⁹ is often carried out: the variables r , p , and E_t are chosen randomly from their appropriate distributions and trajectories run to see whether $\chi_{b \leftarrow a}(P, R, p, r)$ is 1 (a reactive trajectory) or 0 (a non-reactive trajectory).

It is not necessary, however, to choose the dividing surface in the reactant region as was done above. Equation 1 is, in fact, rigorously independent of the particular choice of dividing surface;² it is only necessary that the surface be one through which all reactive trajectories must pass. Figure 1 shows two other possible choices, surfaces S_2 and S_3 . This independence of the choice of dividing surface is a consequence of the classical continuity equation (i.e., Liouville's theorem); this theorem states that if the surface defined by the equation

$$f(\mathbf{q}) = 0$$

is a closed surface and if the distribution function $\rho(\mathbf{p}, \mathbf{q})$ is constant along a classical trajectory, then

$$\int d\mathbf{p} \int d\mathbf{q} \rho(\mathbf{p}, \mathbf{q}) \delta[f(\mathbf{q})] \frac{\partial f(\mathbf{q})}{\partial \mathbf{q}} \cdot \mathbf{p}/m = 0 \quad (7)$$

in words, eq 7 states that the steady-state flux through a closed surface is zero. Equation 1 corresponds to the distribution function

$$\rho(\mathbf{p}, \mathbf{q}) = e^{-\beta H(\mathbf{p}, \mathbf{q})} \chi_{b \leftarrow a}(\mathbf{p}, \mathbf{q}) \quad (8)$$

conservation of total energy implies that $H(\mathbf{p}, \mathbf{q})$ is

constant along a trajectory, and it is clear from the definition of $\chi_{b \leftarrow a}(\mathbf{p}, \mathbf{q})$ that it also is (if the trajectory determined by (\mathbf{p}, \mathbf{q}) is reactive at one time it obviously cannot be otherwise at another time), so that the distribution function in eq 1, eq 8, satisfies the condition of the theorem. Furthermore, it is clear that in Figure 1 surfaces S_1 and S_3 , for example, can be made into one closed surface by joining them with segments at infinity. By the classical continuity equation, the flux through this closed surface is zero. Since no flux passes through the pieces of the surface at infinity, this means that the flux into the closed surface through S_1 must be equal to the flux out of the closed surface through S_3 , or equivalently, that the flux in the reactive direction through S_1 must be equal to the flux in the reactive direction through S_3 . This argument is clearly valid for any surface which divides reactant and product space and thus proves the assertion that eq 1 is independent of the particular dividing surface.

The stage is now set to introduce the "fundamental assumption" of transition-state theory (Wigner's¹² third assumption). The goal is to eliminate the characteristic function $\chi_{b \leftarrow a}(\mathbf{p}, \mathbf{q})$ from eq 1, and therefore the need to determine the complete classical dynamics of the system (i.e., to compute classical trajectories), and this is done in the following way. The "fundamental assumption" is that, if the dividing surface is chosen in the appropriate place, then any trajectory which crosses it in the reactive direction is indeed a reactive trajectory, i.e., that it does not subsequently recross the surface and become nonreactive. Put another way, it is the assumption that the dividing surface is one which no trajectory crosses more than once. Whenever this assumption is true, transition-state theory is exact (within the world of classical mechanics presently being considered).^{6a}

To frame it more quantitatively, suppose surface S_3 in Figure 1 is chosen as the one through which one assumes no trajectory passes more than once. (It is clear that surfaces S_1 and S_2 would be poor candidates for such a surface.) It is then convenient to choose the two coordinates to be s and u as depicted in Figure 1, and the dividing surface S_3 then corresponds to the following function $f(s, u)$,

$$f(s, u) = s \quad (9)$$

i.e., $s = 0$ defines surface S_3 . Equation 1 for the exact classical rate constant then reads

$$k_{b \leftarrow a} = Q_a^{-1} h^{-2} \int_{-\infty}^{\infty} dp_s \int_{-\infty}^{\infty} du \int_{-\infty}^{\infty} dp_u \times e^{-\beta H(p_s, s, p_u, u)} \left(\frac{p_s}{m_s} \right) \chi_{b \leftarrow a}(p_s, s, p_u, u) \quad (10)$$

with $s = 0$. The "fundamental assumption" of transition-state theory corresponds to the replacement

$$\chi_{b \leftarrow a}(p_s, s, p_u, u) \rightarrow h(p_s) \quad (11)$$

where $h(x)$ is the step-function:

$$h(x) = \begin{cases} 1, & x > 0 \\ 0, & x < 0 \end{cases}$$

i.e., it is assumed that if the trajectory has positive momentum in the reactive direction at the dividing surface, then it is indeed reactive in the $a \rightarrow b$ direction. Since the total Hamiltonian is of the form

$$H(p_s, s, p_u, u) = \frac{p_s^2}{2m_s} + \frac{p_u^2}{2m_u} + V(s, u) \quad (12)$$

where $V(s, u)$ is the potential-energy surface, eq 10 becomes

$$k_{b \leftarrow a} = Q_a^{-1} \left[h^{-1} \int_{-\infty}^{\infty} dp_s h(p_s) \frac{p_s}{m_s} e^{-\beta p_s^2 / 2m_s} \right] \\ \times \left[h^{-1} \int_{-\infty}^{\infty} dp_u \int_{-\infty}^{\infty} du e^{-\beta [(p_u^2 / 2m_u) + V(0, u)]} \right] \\ = \frac{kT}{h} \frac{Q^\ddagger}{Q_a} e^{-\beta V_0} \quad (13)$$

where $V_0 = V(0, 0)$ and Q^\ddagger is the classical partition function of the "activated complex", the system with one degree of freedom removed:

$$Q^\ddagger = h^{-1} \int_{-\infty}^{\infty} dp_u \int_{-\infty}^{\infty} du \\ \times e^{-\beta [(p_u^2 / 2m_u) + V(0, u) - V(0, 0)]} \quad (14)$$

By invoking eq 11, the "fundamental assumption" of transition-state theory, all explicit reference to classical dynamics (i.e., to the characteristic function $\chi_{b \leftarrow a}$) is therefore eliminated, and one recognizes eq 13 as the usual expression for the rate constant in transition-state theory.^{1,14}

In concluding this discussion of classical transition-state theory it is interesting to note how different this dynamical view of transition-state theory à la Wigner¹² is from other presentations which refer to the following "mechanism"



to derive eq 13. It is often implied that some sort of equilibrium between reactants and "activated complexes" is responsible for the ratio of partition functions that appear in eq 13. This in turn suggests that transition-state theory should perhaps be most applicable if A and BC form a collision complex that lives for many vibrational periods. (Recall the desire in the early days of transition-state theory for the H + H₂ potential surface to have a well at the top of the barrier.) The discussion in the above paragraphs shows, on the contrary, that the fundamental assumption of transition-state theory is that the mechanism is "direct", that all trajectories move right across the dividing surface and do not return. This assumption of "straight-through" dynamics is essentially the opposite to that of a long-lived collision complex, for the latter would result in trajectories which recross the dividing surface many times and thus invalidate the "fundamental assumption".

Accuracy of Classical Transition-State Theory

Before considering quantum mechanical transition-state theory, it is useful to look at the accuracy of classical transition-state theory, i.e., the validity of the "fundamental assumption" that no trajectories cross the dividing surface more than once, that the reaction dynamics is "direct". Thus consider a simple collinear reaction such as H + H₂ → H₂ + H with the dividing surface chosen as the symmetric line (surface S₃ in

Figure 1). It also simplifies matters to consider the *microcanonical* version of transition-state theory, which corresponds to a fixed total energy E rather than a fixed temperature T . The dimensionless function $N(E)$ is defined by

$$N(E) = 2\pi\hbar h^{-F} \int dp \int dq \delta[E - H(\mathbf{p}, \mathbf{q})] \\ \times \delta[\mathbf{f}(\mathbf{q})] \frac{\partial \mathbf{f}(\mathbf{q})}{\partial \mathbf{q}} \cdot \mathbf{p} / m \chi_{b \leftarrow a}(\mathbf{p}, \mathbf{q}) \quad (16)$$

in terms of which it is easy to see that the rate constant in eq 1 is given by

$$k_{b \leftarrow a} = Q_a^{-1} (2\pi\hbar)^{-1} \int_0^\infty dE e^{-\beta E} N(E) \quad (17)$$

The transition-state approximation to $N(E)$ corresponds to replacing $\chi_{b \leftarrow a}$ in eq 16 by the approximation in eq 11.

$N(E)$ is clearly 0 for $E < V_0$, V_0 being the position of the saddle point in the potential-energy surface, for no classical trajectory can be reactive unless it has enough energy to go over the barrier. For total energies E only slightly above the barrier it is not hard to conclude that the transition-state approximation for $N(E)$ will be *exact*,^{6a} i.e., there will be no trajectories which cross the dividing surface more than once. To see this, imagine beginning a trajectory on the symmetric line with a total energy only slightly above the saddle point; the trajectory will begin slowly, pick up speed as it runs down the hill toward products, and clearly not return. At sufficiently high energy, on the other hand, it is clear that there will be trajectories which rebound back across the symmetric line and thus invalidate the "fundamental assumption".

Since the transition-state approximation to $N(E)$ begins correctly at the classical threshold V_0 , the primary question in classical transition-state theory is how high above V_0 can E be increased and it still be true that there are no recrossing trajectories. Pechukas and McLafferty^{6a} have made an ingenious contribution to answering this question by discovering a simple geometrical criterion for finding a critical energy below which the transition-state approximation to $N(E)$ is exact. Another approach to investigating this question is the "experimental" one of simply comparing the exact $N(E)$ function, determined by carrying out classical trajectory calculations, with the transition-state approximation to $N(E)$.

Figure 2 shows such a comparison^{15,16} of the exact and the transition-state approximation for $N(E)$ as a function of total energy for the collinear H + H₂ reaction. As expected, at low energy—up to about 0.3 eV above the barrier height in this case—the transition-state approximation is essentially exact, i.e., there are no trajectories at these energies that recross the symmetric line. At higher energies, however, there do exist trajectories that rebound back across so that the transition-state approximation to $N(E)$ is too large.

Figure 3 shows a similar comparison^{15,16} for the

(15) S. Chapman, S. M. Hornstein, and W. H. Miller, *J. Am. Chem. Soc.*, **97**, 892 (1975).

(16) The functions actually plotted in Figures 2 and 3 are the ratio of $N(E)$, the reactive flux, to the incident flux (or flux per unit area for the three-dimensional case). These ratios have the more physically meaningful interpretation of an average reaction probability in the collinear case (Figure 2) and an average reaction cross section in the three-dimensional case (Figure 3).

(14) A lucid derivation of the classical transition-state-theory rate expression, eq 13, has also been given by Mahan [B. H. Mahan, *J. Chem. Educ.*, **51**, 709 (1974)] using essentially these same physical ideas.

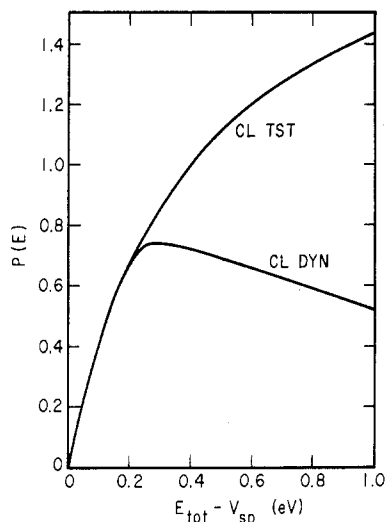


Figure 2. Reaction probability for the collinear H + H₂ reaction on the Porter–Karplus potential surface from a microcanonical classical trajectory calculation (CL DYN) and microcanonical classical transition-state theory (CL TST), as a function of total energy above the barrier height (1 eV = 23.06 kcal/mol).

three-dimensional H + H₂ reaction, the exact $N(E)$ being evaluated by Monte-Carlo trajectory calculations. Again one sees that transition-state theory is essentially exact for energies up to about 0.3 eV above the barrier, and even when it begins to fail it is in much less error than in the collinear case; at 1 eV above the barrier the transition-state approximation to $N(E)$ is only 10% too large.

The above relation between the collinear and three-dimensional H + H₂ reaction (both with the same Porter–Karplus¹⁷ potential-energy surface) illustrates a feature which one expects to be general, namely that, other things being equal, the fundamental assumption of transition-state theory is better the higher the dimensionality of the system. This is understood qualitatively in that fewer trajectories, having departed from the dividing surface toward products, are able to find their way back in the higher dimensional phase space; i.e., they are more likely to get “lost” and not return.

Toward a Quantum Transition-State Theory

The previous sections have shown that within the realm of classical mechanics transition-state theory describes the threshold region of the reactive cross section quite accurately. This success of classical transition-state theory is somewhat hollow, however, because quantum effects are important in the threshold region, particularly so if the reactive dynamics involves light atoms (i.e., H atom transfer). The task, then, is to implement the “fundamental assumption” of transition-state theory in a fully quantum mechanical framework.

There are several reasons for believing that the assumption of “direct dynamics” through the saddle point region is valid for the threshold region also in a quantum mechanical theory. The streamlines of flux computed by Kuppermann et al.¹⁸ for the H + H₂ reaction, for example, show “straight-through” dynamics at low energy, even in the tunneling regime below the classical

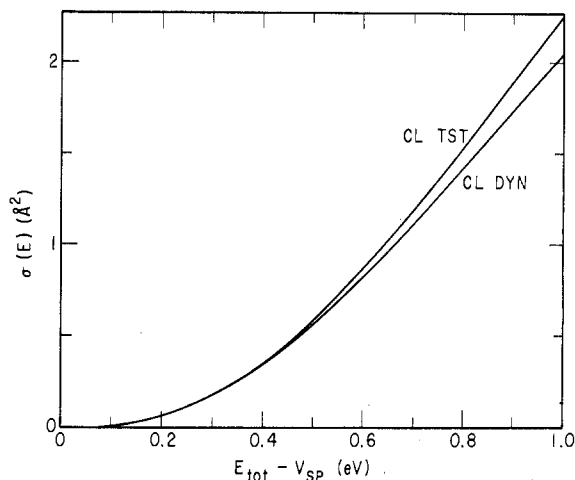


Figure 3. Same as in Figure 1, except that $\sigma(E)$ is the microcanonical reactive cross section for the three-dimensional H + H₂ reaction.

threshold. (At higher energies, though, the streamlines develop “whirlpool effects”, corresponding to recrossing classical trajectories.) Similarly, the semiclassical calculations of George and Miller¹⁹ show complex-valued classical trajectories which tunnel “straight through” the saddle point region.

The first step in constructing a quantum version of transition-state theory is to write the exact quantum mechanical expression for the rate constant (assuming a Boltzmann distribution of reactants). This can be expressed in a number of ways, but the form most useful for present purposes is one⁷ which is the direct analog of the classical expression in eq 1,

$$k_{b \leftarrow a}(T) = Q_a^{-1} \text{tr} \left[e^{-\beta H} \delta(f) \frac{\partial f(\mathbf{q})}{\partial \mathbf{q}} \cdot \mathbf{p} / m \mathcal{P} \right] \quad (18)$$

where tr means a quantum mechanical trace, the quantum analog of a classical phase space average; H , $f(\mathbf{q})$, and \mathbf{p} all have the same meanings as in eq 1 except that they are now quantum mechanical operators. The projection operator \mathcal{P} is the quantum analog of the characteristic function $\chi_{b \leftarrow a}$ in eq 1, and it is given explicitly by⁷

$$\mathcal{P} = \lim_{t \rightarrow -\infty} e^{iHt/\hbar} h(-P) e^{-iHt/\hbar} \quad (19)$$

P being the momentum operator conjugate to R . The appearance of the quantum mechanical evolution operator, $e^{-iHt/\hbar}$, in \mathcal{P} shows that it is the factor which contains all the quantum scattering dynamics, analogous to the dynamical content of the classical function $\chi_{b \leftarrow a}$. In words, \mathcal{P} projects onto all states that have evolved in the infinite past from reactants.

As in the classical case, one can show⁷ that the exact quantum rate constant in eq 18 is independent of the specific choice of the dividing surface. Quantum transition-state theory is thus defined in a manner analogous to the classical case: a specific choice is made for the dividing surface (e.g., surface S_3 in Figure 1), and then the “dynamical factor” \mathcal{P} is approximated by invoking the fundamental assumption of transition-state theory. Analogous to eq 11, one makes the replacement

$$\mathcal{P} \rightarrow h(p_s)$$

this approximate projection operator projects onto all states that have positive momentum in the s direction,

(19) T. F. George and W. H. Miller, *J. Chem. Phys.*, **56**, 5722; **57**, 2458 (1972).

(17) R. N. Porter and M. Karplus, *J. Chem. Phys.*, **40**, 1105 (1964).

(18) A. Kuppermann, J. T. Adams, and D. G. Truhlar, in “Electronic and Atomic Collisions”, Abstracts, VIII ICPEAC, B. C. Cobic and M. V. Kurepa, Ed., Institute of Physics, Belgrade, Yugoslavia, 1973, pp 149–150.

and it is the "fundamental assumption" that positive momentum in the s direction at the dividing surface implies evolution from reactants in the infinite past.

This approach⁷ to quantum mechanical transition-state theory thus gives the rate constant as

$$k_{b \leftarrow a} = Q_a^{-1} \text{tr} \left[e^{-\beta H} \delta(s) \frac{p_s}{m_s} h(p_s) \right] \quad (20)$$

If one does introduce the assumption that the Hamiltonian is *separable* in s and u coordinates,

$$H = h_s + h_u + V_0 \quad (21)$$

then it is easy to show⁷ that the conventional expression for the rate constant results

$$k_{b \leftarrow a} = \Gamma \frac{kT}{h} \frac{Q^\ddagger}{Q_a} e^{-\beta V_0} \quad (22)$$

where Q^\ddagger is the quantum mechanical partition function of the "activated complex"

$$Q^\ddagger = \text{tr}_u (e^{-\beta h_u}) \quad (23)$$

and Γ is a one-dimensional tunneling coefficient,

$$\Gamma = 2\pi\hbar\beta \text{tr}_s \left[e^{-\beta h_s} \delta(s) \frac{p_s}{m_s} h(p_s) \right] \quad (24)$$

The assumption of separability of the Hamiltonian, however, one knows to be a poor approximation in the threshold region where quantum effects are important. One manifestation of this is the "corner-cutting" effect that has been seen in a number of different kinds of calculations for the $\text{H} + \text{H}_2$ reaction:¹⁸⁻²⁰ at low energies in the threshold region the tunneling from reactants to products "cuts the corner", going through the side of the barrier rather than directly under the saddle point itself. Other evidence for the breakdown of the separability approximation is the gross departure from vibrationally adiabatic behavior in the saddle-point region seen in the study of Bowman et al.,²¹ as well as the poor agreement that eq 22 gives with the exact quantum scattering calculations of Truhlar and Kuppermann.¹⁰

To make a fair test of the "fundamental assumption" of transition-state theory in the quantum mechanical case one thus needs to evaluate eq 20 without incorporating any kind of assumption of separability. This is a considerably more difficult task, however, because the Boltzmann operator $e^{-\beta H}$ does not now factor into separate one-dimensional operators.

A first step toward evaluating eq 20 without assuming separability has been made^{22,23} by introducing a semiclassical approximation for the Boltzmann operator and evaluating the trace within the semiclassical limit; no assumptions involving separability, however, are introduced. In addition to simplifying the calculation, the semiclassical limit of eq 20 leads to a very interesting physical picture of the nonseparable tunneling dynamics.

Briefly, the semiclassical approximation to eq 20 gives an expression for the rate constant which is similar in

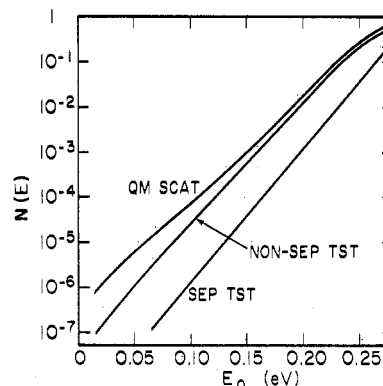


Figure 4. The function $N(E)$, defined by eq 16, for the collinear $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ reaction, as a function of total energy E_0 above the ground state of H_2 . (In this energy regime $N(E)$ is simply the ground-state to ground-state reaction probability.) QM SCAT denotes the (exact) result of quantum scattering theory (ref 24), and SEP TST is that of conventional (i.e., separable) transition-state theory with a one-dimensional tunneling correction.^{10,25} NON-SEP TST is the result based on a semiclassical evaluation of eq 20,²³ the generalized transition-state theory that takes account of nonseparability.

form to the usual separable quantum mechanical expression, eq 22, but with some fundamental differences. First, the tunneling probability P , from which Γ is computed, has the usual semiclassical form

$$P = (1 + e^{2\theta})^{-1}$$

$$\theta = \text{classical action integral} \quad (25)$$

but where the action integral θ is computed along a particular classical trajectory that is determined by the full (nonseparable) dynamics in the saddle-point region and which is in general a different path for different energies. (Specifically, the "tunneling trajectory" is a periodic orbit on the upside-down potential-energy surface!) Thus the region where tunneling takes place changes with energy and in the same way as the "corner-cutting effect"¹⁸⁻²⁰ mentioned above, i.e., the lower the energy the more the tunneling trajectory "cuts the corner". Second, the energy levels of the "activated complex" are also energy dependent. In ordinary transition-state theory the energy levels from which Q^\ddagger is computed are given (within a harmonic approximation) by

$$\epsilon_n = \hbar\omega^\ddagger(n + 1/2) \quad (26)$$

where ω^\ddagger is the frequency of the stable vibration at the saddle point, and the semiclassical analysis replaces this by

$$\epsilon_n = \hbar\omega(E)(n + 1/2) \quad (27)$$

For high energies the energy-dependent frequency $\omega(E)$ approaches ω^\ddagger , but for low energies in the tunneling region $\omega(E)$ increases with decreasing energy and for very low energies actually approaches the vibrational frequency of the *free* H_2 molecule. (In the semiclassical theory $\omega(E)$ emerges as the stability frequency of the periodic orbit along which tunneling occurs.) The reader more interested in this semiclassical approximation to eq 20 should see the original papers.^{22,23}

Figure 4 shows the comparison of the "exact" function $N(E)$, obtained from quantum scattering calculations,²⁴ to that obtained by this semiclassical evalua-

(20) See also E. M. Mortensen and K. S. Pitzer, *Chem. Soc., Spec. Publ.*, No. 16, 57 (1962); R. A. Marcus, *J. Chem. Phys.*, **45**, 4493 (1966); E. A. McCullough and R. E. Wyatt, *ibid.*, **54**, 3578 (1971).

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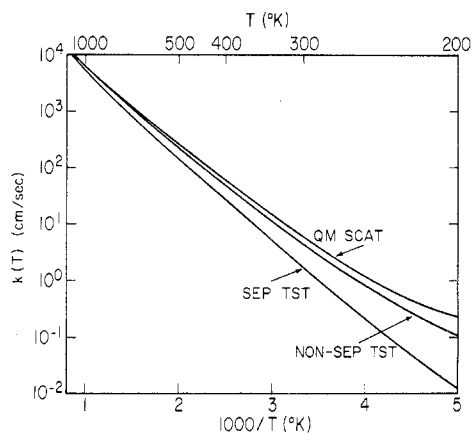


Figure 5. Rate constant as a function of temperature for the collinear $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ reaction; the labels have the same meaning as in Figure 4. These results were calculated by eq 17 with the $N(E)$ functions in Figure 4. The units of $k(T)$ are cm/s (velocity times reaction probability) because the three atoms are all required to move along a line; if they were allowed to move in a plane or in three-dimensional space, then the units would be cm^2/s (velocity times length) or cm^3/s (velocity times area, or cross section), respectively.

tion²³ of eq 20, again for the collinear $\text{H} + \text{H}_2$ reaction. Also shown is the result for $N(E)$ given by conventional (i.e., separable) transition-state theory with a one-dimensional tunneling correction.^{10,25} The comparison of the corresponding rate constants as a function of temperature, obtained from the functions $N(E)$ via eq 17, is shown in Figure 5.

The results in Figures 4 and 5 show quite clearly the degree to which the separability approximation fails in the threshold region. They also show that once nonseparability is properly taken into account, quantum mechanical transition-state theory provides a good description of the threshold region and thus the rate constant.

Conclusions and Prognosis

Although one should be wary of drawing too many conclusions from only one example, a few seem safe. For the threshold region of a simple chemical reaction it does seem that the "fundamental assumption" of transition-state theory is accurate quantum mechanically, as it is classically, *provided* the separability approximation is not introduced to simplify the quantum calculation. Since the effects of nonseparability, and quantum effects in general, are probably more prominent in the collinear $\text{H} + \text{H}_2$ reaction discussed in the previous sections than in any *real* chemical reaction, it

indeed provides a severe test. Thus the generalized definition of quantum mechanical transition-state theory is seen to be a useful and accurate one (although there are some subtle ambiguities⁷ not discussed here).

For the future one needs to explore other ways of evaluating eq 20 and to investigate the effects that nonseparability might have for real chemical reactions; e.g., are they negligible except perhaps for H-atom transfer reactions? Even more interesting is the question of how one can define transition-state models for chemical reactions which do not have a single saddle point separating reactants and products. Suppose, for example, the triatomic molecule $\text{A}-\text{B}-\text{C}$ has a stable potential well with two different saddle-point regions leading to either $\text{AB} + \text{C}$ or $\text{A} + \text{BC}$. The $\text{A} + \text{BC}$ collision would then likely lead to a collision complex (if the reaction is not too endo- or exothermic) which would invalidate the simple version of the "fundamental assumption" of transition-state theory. By considering *two* dividing surfaces, however, drawn through the two saddle-point regions, it is possible to develop a transition-state model by assuming the flux through each of the two surfaces individually is direct. Recently,²⁶ in fact, it has been possible to define a more general statistical theory which includes both the limit of "direct" dynamics that is described correctly by simple transition-state theory and also this opposite limit, a long-lived collision complex, which is described correctly by the "phase space model" of Light.²⁷ It may thus be possible to employ transition-state-like approximations to a much wider class of chemical reactions than only those for which simple transition state theory is appropriate.

Another recent and very interesting direction²⁸ is use of the fundamental assumption of transition-state theory to simplify quantum mechanical scattering calculations by imposing boundary conditions on the scattering equations that take advantage of the "direct" nature of the dynamics in the saddle-point region. Also of importance is the extent to which transition-state models can be developed for describing nonadiabatic reactions,²⁹ i.e., chemical reactions involving more than one potential-energy surface.

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(25) There are a variety of prescriptions considered in ref 10 for how to calculate the one-dimensional tunneling coefficient Γ in the conventional quantum mechanical version of transition state theory. That plotted in Figure 5 is the "vibrationally adiabatic zero curvature" model which is perhaps most justifiable theoretically. Other prescriptions tried in ref 10 give no better results.

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