VARIATIONAL TRANSITION STATE THEORY

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INTRODUCTION

Transition state theory (TST)[1] is the most widely used theory for calculating
rates of bimolecular reactions occurring in the gas phase and in condensed
phases. TST is also incorporated into the widely used RRKM theory for
unimolecular reactions. The popularity of TST is largely due to its
simplicity and its usefulness for correlating trends in reaction rates in terms
of easily interpreted quantities. Several forms of variational transition state
theory (VTST) have been proposed, one as early as 1937; however, until
recently, most applications of TST have been limited to the conventional
(nonvariational) formulation. In recent years there has been renewed
interest in VTST for providing insights into the factors controlling chemical

[1] An alphabetical list of the abbreviations used in this article is as follows : CVT, canonical
variational transition state theory; DA, dynamical-path vibrational-average tunneling
approximation; GTST, generalized transition state theory; ICVT, improved canonical
variational transition state theory; LA, least-action tunneling approximation; LAG, least-
action ground-state transmission coefficient; LC, large-curvature tunneling approximation;
LCG, large-curvature ground-state transmission coefficient; MCP, Marcus-Coltrin path; PA,
phase-average tunneling approximation; RRKM, Rice-Ramsperger-Kassel-Marcus; SAG,
semiclassical vibrationally(-rotationally) adiabatic ground-state transmission coefficient; SC,
small-curvature tunneling approximation; SO, second-order tunneling approximation; SOP,
semiclassical optical potential tunneling approximation; TST, transition state theory; US,
unified statistical model; VA, vibrational-average tunneling approximation; VTST, vari-
ational transition state theory; μVT, microcanonical variational transition state theory.

reaction rates, and VTST has been developed into a practical quantitative tool. The present review is concerned with the most recent developments, and we shall aim to complement rather than duplicate several other recent reviews, which we now summarize.

Chesnavich & Bowers (30, 31) reviewed applications of statistical methods in gas-phase ion chemistry, including detailed discussions of transition-state switching models and applications of VTST to ion-dipole capture. Walker & Light (188) reviewed the theory of reactive collisions, including progress to date on VTST. Truhlar & Garrett (173) provided an introduction to VTST and an overview of their early work on the subject. Two later articles, by Garrett et al (67) and Truhlar et al (181), provided partial reviews of selected aspects of further work of this group; these articles are partly review and partly new material, and they are discussed further below. Pechukas (124, 125) reviewed recent developments in transition state theory, including VTST, and we especially wish to single out his discussions of quantal and semiclassical approaches and of periodic-orbit dividing surfaces. Pollak (138) has also reviewed periodic-orbit dividing surfaces and related topics. Laidler & King (95) reviewed the historical origins of transitions state theory, excluding VTST, with coverage up to about 1938; Hirschfelder (81) provided additional historical comments. Hase (79) reviewed the history and use of variational concepts in unimolecular rate theory. Truhlar et al (177) reviewed the current status of transition state theory, including VTST, with special emphasis on the validity of the equilibrium and dynamical bottleneck assumptions, on localized states in unimolecularly decaying systems, and on frictional effects in solution-phase reactions. Truhlar et al (180) wrote a handbook-type chapter and concentrated on the practical aspects of VTST calculations, with emphasis on reactions of polyatomics, anharmonicity, tunneling, and other corrections. See (200) on TST and VTST, emphasizing organic applications.

The present review of VTST concentrates on work reported since the previous review in this series, by Pechukas (124). Readers are referred to Garrett & Truhlar (56) and to the reviews mentioned above for more extensive references to earlier work. We also restrict the present review to gas-phase reactions.

In addition to variational transition state theory, this chapter briefly considers relevant recent developments in selected aspects of several related subjects: related dynamical theories, the role of tunneling in chemical reactions, the calculation of dynamical bottlenecks and rate constants for state-selected processes, the role of resonances in chemical reactions, and vibrational bonding.

BASIC CONCEPTS

Since VTST is introduced in several of the papers above, we give here only a brief review as background to the later sections.

Transition state theory is a statistical mechanical theory of chemical reaction rates that may be derived from two fundamental assumptions. First one defines a reaction coordinate s leading from reactants (negative s) to products (positive s) and a (generalized) transition state as a system part way between reactants and products with a fixed value for s (thus the transition state is a system with one less degree of freedom than the reactants). The first assumption is that transition state species that originate as reactants are in local equilibrium with reactants. The second assumption is that any system passing through the transition state does so only once (before the next collision or before it is stabilized or thermalized as a reactant or product). These assumptions may be called the *local-equilibrium* and *no-recrossing* assumptions. Early workers were aware that the validity of the no-recrossing assumption depends on the location of the transition state, and that the transition state may be variationally defined as the phase-space hypersurface with the least one-way flux through it (82, 192) or as the hypersurface that yields the smallest free energy of activation (48). But in all conventional formulations of transition state theory, the transition state passes through a saddlepoint on a potential energy surface and the omitted coordinate s is taken as the unbound saddlepoint normal mode (49). Variational transition state theory (VTST) is the name we apply to theories that use the minimum-flux or maximum-free-energy-of-activation criteria to choose the transition state. VTST does not provide exact expressions for rate constants because it still involves the local-equilibrium assumption and because additional approximations are required to translate the flux-through-a-hypersurface argument into practical terms in a quantum mechanical world. Furthermore the variational search for the best transition state is usually carried out with constraints (e.g. one-dimensional search in coordinate space) for practical reasons.

Although the early statements of the classical variational principle by Wigner (192) and Horiuti (82) are correct and clear, the reader should be warned that there has also been some confusion about VTST. Thus Evans (48) incorrectly implied that the maximum free energy of activation corresponds to a minimum-probability rather than a minimum-flux condition and that the minimum-free-energy transition state passes through the saddlepoint. Later workers sometimes confused the minimum-flux condition with a minimum-density-of-states condition. Some workers attempted to discuss variational ideas in terms of free energy surfaces as

functions of more than one coordinate, whereas the free energy to be minimized is a function of the location of a transition state surface, not a function of all the coordinates of the system. For another example, Swarc (169) provided a correct description of how to carry out a maximum-free-energy-of-activation calculation with classical reaction-coordinate motion, but Eyring (50) commented incorrectly that it is not possible to define the free energy of activation if the transition-state hypersurface does not pass through a stationary point of the potential energy, i.e. the saddlepoint. Swarc himself was unsure how to compare calculations with different reaction coordinates, but correct appreciation of the variational criterion shows that it applies to arbitrary variations in the transition state, not just to different choices for a given reaction coordinate.

Modern appreciation of VTST concepts includes the discussion of Eliason & Hirschfelder (47) of the relationship of a variational criterion for the transition-state-theory rate constant to collision theory and the applications by Keck (89, see also 90) of variational theory to atom-atom recombination in the presence of a third body. Keck (91) also presented variational theory in a more general context. Bunker & Pattengill (23), Marcus (102, 103), and Wong & Marcus (196) proposed related schemes (not VTST) for unimolecular and bimolecular reactions (see also 55, 56, 171). Tweedale & Laidler (185) provided an example of a free-energy-of-activation curve as a function of reaction coordinate for a collinear atom-diatom reaction, and Quack & Troe (145–149) used VTST and related dynamical schemes for a series of calculations on unimolecular decompositions of triatomics. In the last five years or so there has been considerable activity in elucidating the classical mechanics of variational transition states; general techniques have been proposed for calculating free energy of activation profiles from potential energy surfaces and for performing VTST calculations for arbitrary systems; and variational transition state theory including important quantization and tunneling effects has begun to receive extensive testing as a general practical tool for for the calculation of bimolecular rate constants.

Some comments on notation: Transition state theory (TST) refers to conventional, generalized, or variational transition state theory. When it is necessary to make a distinction, conventional transition state theory refers to placing the transition state at a saddlepoint on the potential energy surface, generalized transition state theory (GTST) refers to arbitrary locations of the transition state, and variational transition state theory refers to GTST when the location of the transition state is determined variationally. The optimum transition states for microcanonical or canonical ensembles correspond to a minimum sum of states or a maximum free energy of activation, respectively. Microcanonical variational theory (μVT)

and canonical variational theory (CVT) denote the results obtained making the transition-state theory assumption at the globally best dynamical bottleneck for a microcanonical or canonical ensemble (55–57). Improved canonical variational theory (ICVT) refers to using μVT below the μVT energy threshold and optimizing the variational transition states for the non-zero contributions based on a canonical ensemble truncated from below at the threshold energy (61, 70).

When TST is compared to gas-phase experimental results, one tests both fundamental assumptions as well as the potential energy surface. When classical TST is tested against accurate classical dynamics (trajectories), one makes the same local-equilibrium approximation and uses the same potential energy surface for both calculations; hence only the no-recrossing assumption is tested. When quantized TST is tested against accurate (i.e. converged) quantal dynamical calculations one again uses the local-equilibrium assumption and the same potential energy surface in both cases, but now one tests not only the implicit translation of the classical no-recrossing assumption to a quantum mechanical world but also the accuracy of the incorporation of quantal effects such as tunneling into the TST calculation.

CLASSICAL VARIATIONAL TRANSITION STATE THEORY

The fundamental TST dynamical assumption of no recrossing is inherently a classical approximation, and classical TST can be formulated invoking the fundamental equilibrium and dynamical assumptions without any ambiguity or further approximations. In classical mechanics, TST provides an upper bound on the cross section or the local-equilibrium rate constant, and this bound is the basis for classical VTST, in which the calculated cross section or rate constant is minimized with respect to the location of the transition state. Physically one interprets the generalized transition states as tentative dynamical bottlenecks to the phase-space flow of trajectories from reactants to products. The variational transition state is the best dynamic bottleneck for an equilibrium ensemble.

For collinear atom-diatom reactions, the classical microcanonical variational transition states are periodic trajectories that vibrate between two equipotentials in the interaction region (123, 124, 138). Such trajectories (called pods) may be found numerically. Pechukas (123, 124) and Pollak (128, 135) have discussed the problems with generalizing the pods treatment to reactions in three dimensions. More approximate but more general techniques for variationally optimizing transition states, straightforwardly applicable in any number of dimensions, involve modeling

the vibrational and rotational state sums (classical phase space volumes) of generalized transition states by the usual techniques of bound-state theory and searching numerically for the optimum transition states (56, 109).

Before 1979, most tests of the accuracy of the TST no-recrossing assumption were carried out for collinear $H + H_2$ with the conventional transition state location at the saddlepoint (26, 27, 78, 127, 166). These studies showed that this assumption is exact for this system up to about 0.2 eV above the barrier for collinear reactions and in 3D the agreement is better than 10% up to 1 eV above the barrier. More recently, both conventional TST and VTST have been compared to accurate classical calculations for a variety of collinear atom-diatom reactions. These studies show that VTST often provides significant improvements in accuracy as compared to conventional TST (142, 167, 56, 61).

These tests of classical VTST against accurate classical rate constants have been for bimolecular reactions with a single saddlepoint. Although more than one dynamical bottleneck can occur for single-saddlepoint reactions because of the decrease in the bound vibrational frequency in going from reactants toward the saddlepoint (an entropic effect), the presence of the two dynamical bottlenecks is an energetic effect for two-saddlepoint surfaces. Garrett et al (68) tested VTST for a potential energy surface with two identical saddlepoints. The second saddlepoint makes the no-recrossing assumption less valid at the first saddlepoint. In fact, TST and μVT overestimate the exact classical rate constant by a factor of two at total energies infinitesimally above the saddlepoint energy. However, the calculations show that the μVT and conventional TST results overestimate the exact classical one by only 20% at an energy 0.1 kcal/mol above the saddlepoint. Over a temperature range from 100 to 10,000 K, conventional TST rates agree with μVT and CVT ones to within 10%. For the system studied, the worst agreement between any form of TST and the exact classical results is for conventional TST at high temperature; for example at 2400 K conventional TST is too high by 21% and at 10,000 K it is too high by 47%.

Wolf & Hase (194) applied minimum-state-density criteria, which are similar to VTST, to find critical configurations for RRKM calculations on the dissociation of H–C–C model systems. The variational RRKM rate constants were larger than those computed from trajectories, typically by a factor of two for the tighter transition states and by factors of 5–50 for the looser cases. The largeness of the latter is probably due to the use of harmonic, separable approximation for the classical density of states and to an oversimplified treatment of the hindered-rotor degrees of freedom.

J. Miller (111, see also 112) has applied classical generalized TST to a reaction with no intrinsic barrier: $H + O_2$. In these calculations, the

harmonic-oscillator, rigid-rotor approximation is used to evaluate the sum of states at the generalized transition state and the density of states of reactants. The vibrational frequencies and moments of inertia are obtained from an ab initio potential energy surface. Although reaction cross sections were computed for several locations of the dividing surface, the location of the dividing surface that gives the minimum reaction cross section for each energy was not found. Using the dividing surface that gives the smallest cross sections, the generalized TST results severely underestimate the quasiclassical trajectory results at all total energies below about 33 kcal/mol. However, we emphasize that these comparisons are for purely classical generalized TST versus trajectories with quantized initial conditions; hence no definite ordering of the resulting cross-sections should be expected.

Martin & Raff (109) have suggested a general procedure for classical variational transition state theory calculations in atom-diatom reactions in three dimensions. The dividing surface is expressed as a linear combination of internal coordinates and the coefficients in this expansion are variationally optimized to minimize the thermal rate constant. Calculations were performed for the $H + H_2$ and $H + I_2$ reactions. For the $H + H_2$ system the variational TST results are within 22% of the exact classical ones over a temperature range 300 to 1100 K. The agreement is not as good for the $H + I_2$ system, in which the VTST result overestimates the classical trajectory rate by a factor of 2.3 at 600 K. By carrying out combined-phase-space-trajectory calculations (4, 85) at their best dividing surface, a factor of 18 reduction in computer time with a decrease of a factor of four in statistical uncertainty was realized for the $H + H_2$ system, as compared to a trajectory calculation with sampling in the reactants' region.

Classical variational transition state theory has also been applied to the calculations of capture rate constants in collisions of ions with polar molecules. Su & Chesnavich (165) have extended earlier calculations (32, 33) to reduce the numerical error. The systems studied corresponded to H^- and H_3^+ reacting with a variety of polar molecules. For these systems the μVT rate constants agree very well with classical trajectory ones.

Swamy & Hase (168) have carried out similar studies for alkali ions recombining with H_2O. In these studies the agreement between classical trajectory rate constants and μVT ones is not as favorable: for the $Li^+ + H_2O$ system errors of 2.3 were found at 300 and 1000 K, and for the $K^+ + H_2O$ system errors of 2.9 and 6 were found at 300 and 1000 K, respectively. The errors are the result of trajectories that form short-lived collision complexes that are not stabilized by a third-body collision, thus leading to recrossing of the dividing surface.

One difficulty in calculating reliable thermal rate constants is the lack of

potential energy surface information. In VTST the necessary information is the potential energy in a region about the minimum-energy path, whereas in conventional TST only information about the potential near the saddlepoint and in the reactant region is necessary. Truhlar et al (182) have developed methods of interpolating parameters in the reaction-path Hamiltonian between reactants, the saddlepoint, and products. They compared μVT valculations based on interpolation to conventional TST, to μVT using the actual potential energy surface information, and to exact classical rate constants for a symmetric, a nearly symmetric, and two asymmetric collinear atom-diatom reactions. In all cases the μVT results computed using the interpolated potential energy surface information are in good agreement with the μVT results obtained using the actual potential. The interpolation schemes provide useful means of obtaining improved estimates of the rate constants for systems with limited potential energy surface information.

VARIATIONAL TRANSITION STATE THEORY IN THE REAL, QUANTIZED WORLD

VTST calculations in the quantum mechanical world have been carried out using the ansatz that if quantum effects on reaction-coordinate motion, which is responsible for movement from the reactants' region of phase space or state space to the products, are temporarily neglected, it still makes physical sense to minimize the rate constant (57). The intermediate-step quantity involved in this step, a rate constant corresponding to classical reaction-coordinate motion but a quantum mechanical treatment of all other degrees of freedom, has been called the *hybrid rate constant.* Minimizing the hybrid rate constant with respect to dividing-surface location is called quantized VTST. (In a quantized calculation there is usually not a large difference between the results of μVT, CVT, and ICVT calculations; in such cases we can just say VTST.) Quantal effects on reaction-coordinate motion and to some extent even quantal nonseparability of the reaction coordinate can be included, if desired, by multiplying the hybrid rate constant by a transmission coefficient. This generally includes both classically forbidden barrier penetration and nonclassical barrier reflection, but since the former usually dominates it is convenient to call this a tunneling correction.

Microcanonical variational theory for the hybrid rate constant is equivalent to making an adiabatic approximation for all degrees of freedom with respect to the reaction coordinate (56, 57). Thus there is a strong connection between VTST and adiabatic collision theories. By use of the adiabatic analogy or diabatic generalizations, the dynamic bottlenecks of

TST can also sometimes be interpreted as dynamical bottlenecks for state-selected reactions or for the decay of quasibound collisional resonance states.

The most important quantum mechanical effect on reaction-coordinate motion is tunneling. Thus the ability to estimate tunneling probabilities accurately is essential to the accurate use of transition state theory for many reactions. In general the tunneling contribution may be estimated by any semiclassical or quantal method; in some cases the adiabatic approximation mentioned above in conjunction with the classical-reaction-coordinate motion part of the calculation is also useful for the tunneling calculations, and the adiabatic derivation of TST makes it clear how to include tunneling consistently (183, 70). Quantized VTST with semiclassical adiabatic transmission coefficients based on the ground-state s-wave reaction probability is abbreviated VTST/SAG. Two kinds of nonadiabatic transmission coefficients have also been applied as corrections to quantized VTST; these have been called the large-curvature ground-state and least-action ground-state methods, and they lead to results abbreviated VTST/LCG and VTST/LAG.

Although it is not a necessary part of VTST, in our own work we have always considered one-dimensional sequences of generalized-transition-state dividing surfaces orthogonal to a gradient-following-path in mass-scaled coordinates. This choice of dividing surfaces is convenient; it eliminates potential coupling between the reaction coordinate and the other degrees of freedom through quadratic terms, and it promotes the dynamic separability of the reaction coordinate, thus tending to minimize local recrossing effects. Furthermore the use of a gradient-following path in mass-scaled coordinates facilitates the inclusion of internal centrifugal effects in tunneling calculations. An excellent discussion of gradient-following paths and the structure of the Hamiltonian in coordinate systems built on such paths has been given by Natanson (120).

Practical VTST calculations for a quantized world have so far been based on variationally optimizing the hybrid rate constant and adding a tunneling correction (70, 181) because more rigorous extensions of VTST to a quantum mechanical world do not provide a useful bound [see the discussions in (123, 172, 43)]. Pollak (131) has presented a new transition state expression with bounding properties and discussed its expansion in a power series in h. The h expansion is known to be slowly convergent for tunneling contributions. It would be interesting to see whether practical and accurate bounds for real chemical reactions could be obtained from this formulation or whether the formalism provides a practically advantageous way to choose variational dividing surfaces.

Garrett et al (71) tested VTST/SAG calculations for model collinear

reactions with mass combinations $H + FH$ and $D + FD$ and with a low-barrier, twin-saddlepoint potential energy surface by comparison against accurate quantal dynamical calculations. The comparisons showed that VTST/SAG predicts accurate local-equilibrium rate constants within a factor of 1.57 over the 200–7000 K range for the $H + FH$ mass combination and within a factor of 1.42 over the 200–2400 K range for $D + FD$, with the largest errors at the lowest temperature in each case. Employment of fully quantal vibrationally adiabatic tunneling calculations rather than semiclassical ones improved the accuracy. In another series of tests of VTST/SAG calculations against accurate quantal collinear rates, Bondi et al (16) considered the reactions $H + H_2$, $Mu + H_2$, and $Mu + D_2$ at 200–2400 K, using two different potential energy surfaces for two of the mass combinations, for a total of five cases. For $H + H_2$ and $Mu + H_2$ the accuracy was 38% or better over the whole temperature range, but for $Mu + D_2$ the errors were in this range only for $T \gtrsim 500$ K or 800 K, depending on the surface. The accuracy of VTST/SAG calculations for the seven systems discussed in this paragraph is actually slightly worse than typical of that found in 18 previous test cases of VTST/SAG calculations against accurate quantal equilibrium rate constants for collinear systems, as reviewed previously (61, 181, 177). In fact, for 300 K, for the full set of 25 cases the ratio to the accurate quantal equilibrium rate constant of the rate constant calculated by VTST/SAG calculations employing CVT for the VTST part and the small-curvature-tunneling approximation (163) for the SAG part, is in the range 0.49 to 1.54 in 22 cases and in the range 0.62 to 1.30 in 17 cases. In contrast, conventional transition state theory calculations often show large errors in these 25 cases: the ratio of conventional transition state theory rate constants to accurate quantal equilibrium rate constants is in the above two ranges in only seven and five cases, respectively, and even extending the range to 0.4 to 2.5 increases the number of cases to only 13.

For $Mu + D_2$ the VTST/SAG calculation on the most accurate surface decreases the errors from factors of 59, 23, and 1.8 in conventional TST at 200 K, 300 K, and 2400 K to 0.42, 0.49, and 0.92, respectively. These results, like all VTST/SAG calculations mentioned so far, are based on straight-line GTST dividing surfaces with anharmonicity treated by a Morse approximation [the Morse I approximation in the notation of Garrett & Truhlar (56, 57)]. Pollak (138) has shown that more accurate results can be obtained for the $Mu + D_2$ mass combination by semiclassical quantization of pods. Straight-line dividing surfaces for collinear reactions have more straightforward three-dimensional and polyatomic analogs than do pods, so we prefer this treatment to one based on pods; but it is not too impractical to go beyond the Morse approximation for anharmonicity. If the anharmonic

energy levels of the straight-line generalized transition states are calculated numerically by the WKB approximation, without the Morse approximation, VTST/SAG agrees with quantal equilibrium rate constants for $Mu + D_2$ on the most accurate surface within 8% over the 200–2400 K temperature range (Garrett & Truhlar 1984, *J. Chem. Phys.* In press); it is encouraging that it is not necessary to use the curved pods as dividing surfaces to achieve this accuracy. Further work (Garrett & Truhlar 1984, *J. Chem. Phys.* In press) shows that although the Morse approximation usually leads to reasonably good agreement with the WKB approximation for the zero point energy at the variational transition state (quantitative differences are largest for reactions with high zero point energies), using the WKB method for stretching vibrations does provide systematic improvement over that achieved in previously reported tests of VTST/SAG calculations against accurate quantal dynamics. The rest of the VTST-plus-tunneling results discussed in the present section were all obtained by the more convenient Morse approximation for stretches and by a mixed quadratic-quartic approximation (62, 84) for bends that have no cubic anharmonicity.

Bondi et al (16) also predicted three-dimensional rate constants for the $Mu + H_2$ reaction based on the most accurate available potential energy surface, the so-called LSTH [Liu (100), Siegbahn & Liu (157), Truhlar & Horowitz (178)] surface. At 600 K, the ratio of the VTST rate to the TST one is 0.11, the ratio of the VTST/SAG rate to one calculated (15) from full quasiclassical trajectory calculations is 0.065, and the kinetic isotope effect (ratio of the rate for $Mu + H_2$ to that for $H + H_2$) is 0.017. The small values for all three ratios are direct consequences of the large zero point effects for this system and the large dependence of the ground-state stretching energy level of the generalized transition state on the value of the reaction coordinate. Despite the size of this effect, the predicted rate constants at 608 K and 875 K are in good agreement with later experimental values [D. M. Garner and D. G. Fleming 1982, unpublished; cited in (15)]. These calculations involve no empirical elements or adjustable parameters and they are believed to be the first totally ab initio reliable, quantitative predictions of chemical reaction rates. With our present confidence in the reliability of our dynamical calculations for a given potential energy surface, the difficulty of making such predictions for other reactions depends more on future advances in electronic-structure calculations of potential energy surfaces than on further advances in treating the dynamics.

Blais et al (13–15), again using the LSTH surface, compared VTST, VTST/SAG, and quasiclassical trajectory calculations of rate constants and activation energies for $H + H_2$, $D + H_2$, and $Mu + H_2$ to each other at 444–2400 K and to experiment at 444–875 K. The VTST/SAG calculations

are in best agreement with experiment at the lower temperatures because of the importance of tunneling. The most interesting aspect of these calculations is the temperature dependence of the activation energy. For example the activation energy predicted by the VTST/SAG calculations for $D + H_2$ rises from 6.8 kcal/mol at 300 K to 7.5, 9.0, and 14.0 kcal/mol at 444, 875, and 2400 K. The latter two values, at temperatures at which tunneling effects are less important, are in good agreement with trajectory values of 8.7 and 13.9 kcal/mol. Since recrossing errors increase with temperature in classical tests for this kind of system, the agreement of variational transition state theory with full trajectory calculations for the slope of the rate constant at 2400 K is encouraging, especially for using the simpler theory for the important practical problem of extrapolating rate constants to high temperature for combustion applications.

Clary (38) tested VTST/SAG calculations (72) against presumably accurate quantal calculations (35, 37, 38, see also 40) for the three-dimensional $D + ClH$ exchange reaction and three isotopic analogs, with the same potential energy surface used for both sets of calculations so that the comparison provided a test of the dynamical methods. The quantal calculations were performed by a method (35, 36) combining the energy sudden and centrifugal sudden approximations in a way particularly appropriate for the transfer of a heavy particle between two light ones. The VTST/SAG and quantal rate constants for 295 K differed by only 15%, 5%, 25%, and 12% for the four cases studied. Good (but not as good) agreement, an error of 38% for $T \geqslant 300$ K, had also been obtained for the only previous test (70, 181), for $H + H_2$, of VTST/SAG calculations against presumably accurate three-dimensional rate constants (156) for a given potential energy surface. Note that for $H + H_2$ no sudden approximations were made in the quantal calculations; the accurate calculations are possible in this case because of the lightness of all three atoms, yielding a relatively small number of channels. In the $H + H_2$ case, as for the $H + FH$ case discussed above, the agreement is considerably improved if fully quantal one-dimensional tunneling calculations (60; see also 124, 173) are substituted for the semiclassical tunneling calculations. Using such fully quantal tunneling calculations, VTST-plus-tunneling results have recently been reported (176) for eight tritium-substituted analogs of the $H + H_2$ reaction, using the accurate LSTH potential energy surface that was also used for the $Mu + H_2$ calculations discussed above.

Clary et al (41) tested VTST/SAG calculations against accurate quantal calculations for collinear $H + BrH$ and $D + BrH$ and against energy-sudden-approximation, centrifugal-sudden-approximation calculations for the same reactions in three dimensions. The VTST/SAG and quantal rate constants showed good agreement in all four cases; e.g. for three-

dimensional H + BrH they agree to 20% or better for 150–500 K, even though the SAG transmission coefficient is 1050 at 150 K.

Garrett et al (72, 73) applied VTST/SAG calculations to three-dimensional kinetic isotope effects in the reactions $Cl + H_2$, D_2, T_2, HD, DH, HT, and TH. They considered eleven different potential energy surfaces with a goal of finding a surface that was consistent with experiment. They found large differences from conventional TST in many cases, especially for intramolecular HD/DH kinetic isotope effects. None of the VTST/SAG calculations was in completely satisfactory agreement with experiment, perhaps because of errors in all the surfaces but also perhaps because of remaining uncertainties in the tunneling calculations or other errors in the dynamics calculations, such as different amounts of recrossing for the different isotopic combinations.

Isaacson & Truhlar (84) extended the VTST formulation to general nonlinear polyatomic reactions and Skodje et al (162) similarly extended the SAG transmission-coefficient approximation. Both extensions make use of the polyatomic reaction-path Hamiltonian of Miller et al (118) and assume independent generalized normal modes. Extensions of these methods have also been presented (180) for three-dimensional polyatomic reactions with linear generalized transition states. Isaacson & Truhlar (84) and Truhlar et al (181) applied the general polyatomic formalism to the reaction $OH + H_2 \rightarrow H_2O + H$, as well as to reactions of OH with D_2, HD, and DH, using Schatz & Elgersma's (155) fit of Walch & Dunning's (186) ab initio potential energy surface. They found that variational optimization of the generalized transition state lowered the calculated rate by a factor of 1.9 at 298 K, and quantal effects on reaction-coordinate motion increased it by a factory of 17 at the same temperature; both the optimization effect and the tunneling correction are decreasing functions of temperature. The final results agree with the recommended experimental rate constants of Cohen & Westberg (42) within a factor of 1.7 over the 298–2400 K temperature range, over which the rate constant varies by a factor of 2×10^3. The calculated results are a factor of 1.6–1.7 higher than experiment (151, 42) at 298 K, a factor of 0.6–0.8 lower at 600 K, and more accurate at 2400 K. Thus they slightly underestimate the low-temperature activation energy and slightly overestimate the high-temperature activation energy. Nevertheless the agreement with experiment is remarkably good. In general one hopes that an ab initio surface is useful for force constants for bound generalized normal modes but one expects to have to adjust the ad initio barrier height to obtain such good agreement with experiment; in this case good agreement was obtained without adjustment. More important is the insight that the VTST/SAG calculation gives into the detailed dynamics. The variational transition states occur 0.07–0.10 a_0 earlier along the reaction

path (in scaled coordinates with a reduced mass of 1.8 amu) than the saddlepoint, curvature of the reaction path increases the SAG transmission coefficient by a factor of 4.3 at 298 K, and the results are sensitive to anharmonicity. The H_2/D_2 kinetic isotope effect is larger than the experimental one (151) at 298–600 K; we may speculate that this and the too-low activation energy at these temperatures occur because the barrier on the potential energy surface is slightly too thin and allows a little too much tunneling, although several other explanations could also be given.

Truhlar et al (174) used a combination of VTST/SAG and trajectory calculations to adjust a new potential energy surface for $F + H_2$ to a variety of experimental data for the reactions $F + H_2$ and $F + D_2$.

Garrett et al (67) presented detailed studies of the trends in variational transition state locations for atom-diatom reactions with a variety of mass combinations and potential energy surfaces, complementing earlier systematic studies (58, 59) of this subject that were limited to rotated-Morse bond-energy-bond-order surfaces. The main conclusions of these studies are as follows. The ratio $k^{\ddagger}/k^{VTST}$ of rate constants calculated by the conventional and variational theories is largest for symmetric or nearly symmetric reactions in which a light particle is transferred between two heavier ones. In these cases the saddlepoint tends to be symmetric or nearly symmetric and small changes in geometry can cause large changes in the zero point energy requirement for a bound stretching coordinate. (There is only one such coordinate for atom-diatom collisions; for polyatomic reactions the analogous stretching coordinate is the one involving atoms participating in the bond changing.) The effect on $k^{\ddagger}/k^{VTST}$ van be very large (up to several orders of magnitude) and decreases with temperature. A second important case is very asymmetric reactions with saddlepoints located well into the reactant or product channel. In these cases the bending effects become dominant. Since potential energy varies more slowly with distance along the reaction coordinate, in these cases the variational transition states may be much farther removed from the saddlepoint and more temperature dependent. The ratio $k^{\ddagger}/k^{VTST}$ increases with temperature in these cases but is usually only a factor of two to three.

In order to provide further evidence that the large $k^{\ddagger}/k^{VTST}$ ratio for symmetric heavy-light-heavy systems are not artifacts of the potential energy surfaces considered, Garrett et al (74) performed VTST calculations for an ab initio potential energy surface for the reactions $^{37}Cl + H^{35}Cl$ and $^{37}Cl + D^{35}Cl$. For three-dimensional $^{37}Cl + H^{35}Cl$ they obtained $k^{\ddagger}/k^{VTST}$ values of 110, 28, and 9 at 200 K, 300 K, and 600 K, confirming the large effect. The saddlepoint on the ab initio surface is symmetric with nearest-neighbor distances at 1.47 Å, potential energy 6.3 kcal/mol, and a bound stretching frequency of 337 cm^{-1}. At the 300 K twin asymmetric variational

transition states, these values are 1.60 Å, 1.35 Å, 5.8 kcal/mol, and 1682 cm^{-1}. Tunneling calculations based on vibrational adiabaticity along the minimum-energy path are not valid for these mass combinations because the minimum-energy reaction path has large curvature in mass-scaled coordinates. Instead, the authors used a new large-curvature tunneling method, leading to the LCG transmission coefficient mentioned above. In order to compare to experiment (92, 93), the surface was scaled along the minimum-energy path (but not orthogonal to it, see the discussion above for the $OH + H_2$ reaction) so that the VTST/LCG rate constant for ^{37}Cl $+ D^{35}Cl$ agreed with experiment at 368.2 K; this yielded a collinear saddlepoint potential energy of 9.0 kcal/mol and a noncollinear saddle-point potential energy about 1.5 kcal/mol lower. The kinetic isotope effects calculated for the scaled surface, as calculated by the conventional TST, VTST, and VTST/LCG methods, are compared to experiment (92) in Table 1. Although both the conventional TST results and the VTST/LCG results are in qualitative agreement with experiment, the physical factor control-ling the kinetic isotope effect is entirely different in the two calculations. In conventional TST this kind of isotope effect is determined by the saddlepoint stretching force constants, as in the widely used Melander-Westheimer model (110, 190). In the VTST calculations without tunneling, the kinetic isotope effect at the temperatures of Table 1 is less than 1.03, so essentially the entire effect in the VTST/LCG calculations is due to quantal effects on reaction coordinate motion. Furthermore, in the LCG model the tunneling for these reactions occurs by rapid light-atom motions at fixed Cl–Cl distance, and most of it occurs for Cl–Cl distances much larger than the Cl–Cl distance at the saddlepoint or even at the outer turning-point distance of the Cl–Cl symmetric-stretch zero-point motion of the conven-tional transition state. These results cast strong doubts on the validity of the common practice in physical organic chemistry of interpreting this kind of isotope effect for H or H^+ transfer in terms of transition state force constants. In a more general context, our VTST calculations call for a critical reexamination of conventional TST interpretations (110) of kinetic isotope effects even in cases when tunneling effects on the kinetic isotope

Table 1 H/D kinetic isotope effects for $^{35}Cl + H^{37}Cl$ on scaled ab initio surface

T (K)	‡	CVT	CVT/LCG	Experimental
368	2.8	1.0	4.2	5.0 ± 0.7
423	2.5	1.0	3.4	4.1 ± 0.4

effect are small because we find in many cases that variational transition states for different isotopic versions of a given reaction are different whereas the basic principle of the conventional analysis is that they are not.

Bondi et al (17) tested the VTST/LCG method against accurate quantal equilibrium rate constants for collinear $Cl + HCl$, $Cl + DCl$, and $Cl + MuCl$, using not the ab initio or scaled ab initio surface but a similar semiempirical surface with a collinear saddlepoint potential energy of 8.55 kcal/mol. The comparison for the $Cl + MuCl$ case is given in Table 2. Both the variational effect, as measured by $k^{\ddagger}/k^{VTST}$, and the quantal effect on reaction-coordinate motion, as measured by $k^{VTST/LCG}/k^{VTST}$, are very large, but the final results are accurate within 39% over a factor of five in temperature. The success of the VTST/LCG method in this case is a consequence of the success of the tunneling calculations. To verify that the VTST part of the calculation is also meaningful, Truhlar, Garrett, Hipes & Kuppermann (1984, *J. Chem. Phys.* In press) tested the same methods against accurate quantal equilibrium rate constants for the reaction $I + HI$ on a low-barrier surface for which tunneling effects are negligible. The results are shown in Table 2, and they verify that the VTST and VTST/LCG methods are reliable for heavy-light-heavy reactions in the low-barrier, no-tunneling limit as well as the high-barrier, tunneling-dominated limit.

So far in this article we have considered primarily tight transition states in which two bonds are simultaneously appreciably partially broken or newly made. Variational transition state theory is also applicable to loose and nearly loose transition states, and we now consider recent papers on that subject.

Cates et al (24) considered the reactions $Cl^+ + H_2 \rightarrow HCl^+ + H$ and $HCl^+ + H_2 \rightarrow H_2Cl^+ + H$. Both reactions are exoergic but the authors found a positive temperature dependence for the former and a negative

Table 2 Ratio of approximate rate constants to accurate quantal equilibrium ones for collinear reactions on semiempirical surfaces

Reaction	T (K)	$\ddagger$	ICVT	ICVT/LCG
$Cl + MuCl$	200	92300	0.003	0.68
	400	581	0.081	1.02
	1000	44	0.56	1.39
$I + HI$	100	17500	0.77	0.77
	200	214	0.99	0.99
	400	96	1.1	1.1
	1000	19	1.4	1.4

temperature dependence for the latter. They interpreted this in terms of an early barrier for the former and, following Farneth & Brauman (51), Olmstead & Brauman (122), Asubiojo & Brauman (5), Jasinski & Brauman (88), and Pellerite & Brauman (129), in terms of a tight variational transition state for the latter. It would be interesting to see whether the latter interpretation could be supported by actual VTST calculations on a full potential energy surface.

Troe (170) provided a simplified version of the statistical adiabatic channel model (145), which is similar to VTST, for unimolecular bond fission reactions and the reverse radical association schemes. This work addresses the difficult question of the correlation of vibrational, rotational, and orbital (centrifugal) energies between the two limits of tight and loose generalized transition states. The properties of the potential energy surface are interpolated by a scheme similar to that originally applied by Quack & Troe (145).

In the section on classical VTST we discussed the work of J. Miller (111) on $H + O_2 \rightarrow HO + O$. This is an endoergic reaction whose dynamical bottleneck lies in the exit channel; it is equivalent but more straightforward to consider the early generalized transition states of the reaction $O + OH$. Rai & Truhlar (150) applied quantized VTST to this case using the ab initio potential energy surface of Melius & Blint (201), and the semiempirical reaction-path correlation scheme of Quack & Troe (148). For the Melius-Blint surface the variational transition state for 300 K occurs at an O-to-OH distance of 5.4 Å, which is much larger than the range of O-to-OH distances for which most of the electronic structure calculations were performed. One advantage of VTST calculations over collision theory calculations is that this kind of information about critical geometries is available and may serve as a guide to future electronic structure calculations so that they may be carried out at the dynamically most important geometries. For 300 K the VTST rate constants, as well as the trajectory calculations of Miller (111), are larger than the experimental rate constants (42), presumably because the ab initio surface is too attractive. It is not clear whether this is a fault of the electronic structure calculations or the extrapolation to large O-to-OH distances. The calculations based on the Quack-Troe scheme were more successful, but it is not known whether this is fortuitous or meaningful, especially since the calculations are sensitive to how the rotational-orbital-motion correlations are treated, and this is quite uncertain.

Clearly further progress on the transition state theory of systems with loose and nearly loose transition states will require better knowledge of potential energy surfaces for such systems. Duchovic et al (45) have recently performed state-of-the-art electronic structure calculations for the poten-

tial energy along the dissociation coordinate in $CH_4 \rightarrow CH_3 + H$. Further work along this line is sorely needed.

VTST concepts have also been applied to a few reactions involving more than four atoms. See the work of Brauman and co-workers mentioned above and also Agmon (1, 2), Chesnavich et al (29), and Jarrold et al (86). Bowers and co-workers proposed a transition-state switching model for ion-molecule reactions involving tight and orbiting generalized transition states. In this model the existence of tight generalized transition states is postulated even for reactions without a saddlepoint; for such reactions there may be a local maximum in the free-energy of activation for tight geometries because, as the system moves along the reaction coordinate in the exoergic direction, rotational-orbital motions of the reactants are converted to vibrations. Such dynamical bottlenecks were found by Garrett & Truhlar (58) for neutral reactions with very small barrier heights in the entrance channel and by Rai & Truhlar (150) for the no-saddlepoint $O + OH$ radical-radical reaction discussed above. As the temperature increases, the canonical variational transition state becomes tighter in such systems; in some cases there may be a tighter and a looser bottleneck even at a single temperature.

The central barriers in long-lived ion-molecule complexes have been further characterized by Wolfe et al (195) and Squires et al (164).

In attempting to use VTST concepts in a qualitative sense one should be careful to distinguish free energies of activation from free energies of formation. Thus, as the generalized transition state tends to reactants or products, it should not be assumed that the free energy of activation tends to zero and to the free energy of reaction, respectively. The difference arises because the free energy of activation is a quasithermodynamic quantity referring to transition states, which are missing one degree of freedom, whereas free energies of reaction and formation include all degrees of freedom.

RELATED TOPICS

Above we have reviewed recent developments in transition state theory. We now briefly consider recent developments in a few closely related subjects. We do not attempt to present self-contained discussions of these subjects in their own context but rather discuss them in relation to VTST concepts.

Related Dynamical Approximations

The unified statistical (US) theory provides a generalization of VTST to the case of two (113) or more (114) dynamical bottlenecks. Unlike VTST, the unified statistical theory does not give a bound even in classical mechanics.

Pollak & Levine [(140, 141), see also Davis (44)] have emphasized that the
US theory for classical systems can be derived by information theory where
the average number of crossings of a critical surface is imposed as a
constraint, and they have also proposed a generalization involving a second
constraint, which may be computed from the entropies of the reactive and
nonreactive state-to-state probability matrices. They (141) also suggested a
canonical generalization by replacing microcanonical fluxes by canonical
ones. A canonical unified statistical theory was also suggested by Garrett &
Truhlar (63), who tested its predictions against accurate classical dynamics
for several collinear atom-transfer reactions. Garrett et al (68) tested the
original classical unified statistical theory against accurate dynamics for a
reaction with two saddlepoints and found that it overestimates the extent
of recrossing and hence underestimates the rate constant. Truhlar et al (180)
discussed the incorporation of quantization and tunneling effects in the
original and canonical unified statistical theories. They also reported that
the quantized canonical unified statistical theory does not systematically
improve on the canonical variational theory in accuracy tests against
accurate quantal equilibrium rate constants for collinear reactions, al-
though it can change predicted kinetic isotope effects by a non-negligible
amount. In the limit of a strongly bound intermediate between the
dynamical bottlenecks, the unified statistical theory reduces to the statis-
tical theory of Pechukas & Light (126) and Nikitin (121). That statistical
theory was originally formulated for loose dynamical bottlenecks so
that the fluxes through the dividing surfaces were proportional to the
asymptotically available phase space, but it was generalized to tight
generalized transition states by Lin & Light (99). Webb & Chesnavich (189)
have used models involving both tight and orbiting transition states in
generalized statistical phase-space theory calculations on the energy
dependence of the cross sections for the reaction $C^+ + D_2$.

Chesnavich (28) proposed a theory related to VTST in which, rather than
varying the dividing surface location, he fixed its location in the entrance
channel and varied its boundary. He obtained upper bounds on cross
sections for atom-diatom exchange reactions.

An important remaining problem in generalized transition state theory is
to estimate recrossing corrections. It would be very convenient if these
could be estimated from local properties of the potential surface. Miller
(114a) attempted to do this using the curvature of the minimum-energy
reaction path at the saddlepoint or the point of maximum curvature;
unfortunately, as discussed elsewhere (180), the predictions of his formulas
do not correlate well with accurate classical dynamics. Global trajectories
provide a more reliable, but more expensive, guide to recrossing effects.
Bowman et al (19) have evaluated transmission coefficients from trajec-

tories starting in asymptotic regions, and Truhlar & Garrett [as discussed in (180, 181)] have evaluated them from trajectories beginning at variational transition states. Further work using this approach is in progress.

Lee, Bowman, and colleagues (18, 97) suggested using reduced-dimensionality accurate quantal calculations to obtain transmission coefficients for full-dimensional TST calculations. In further work, Walker & Hayes (187) and Bowman et al (21) presented reduced-dimensionality calculations for reaction of H with vibrationally excited H_2. The reduction in dimensionality was achieved by treating bending degrees of freedom adiabatically, and it corresponds to using generalized transition state theory for bending and rotational degrees of freedom and full dynamics for the two most strongly coupled degrees of freedom. Miller & Schwartz (119) and Skodje & Truhlar (161) have presented improved system-bath decompositions of reaction-path Hamiltonians that might be used for this kind of approximation.

Kuppermann (94), Christov (34), and Truhlar et al (180) have provided discussions of the relation of transition state theory to accurate collision theory. The goal of this kind of analysis is to provide further insight into the dynamical corrections to TST, such as those considered in the previous paragraphs.

In microcanonical transition state theory one calculates a rate constant for each total energy of the transition state. Miller (115–117) has pointed out that one should calculate a distinct microcanonical rate constant for each irreducible representation of the transition state in the symmetry group that applies along the reaction path, since states of different symmetry are decoupled. The difference between the rate constants for different symmetries is largest for energies near threshold. A related practical point is that it is sometimes better to base transition state theory on a reference path through a saddlepoint with two imaginary frequencies. This kind of reference path has been used for the unimolecular decomposition of H_2CO (116) and for $^{37}Cl + H^{35}Cl$ (74). Celli et al (202) and Sakimoto (203) have calculated ion-dipole capture rate constants using an average-free-energy-function method and an adiabatic method, respectively; both methods are closely related to μVT (31).

Tunneling

As discussed above, accurate transmission coefficients that account for tunneling contributions are an important ingredient in transition state theory calculations for many cases. We have already mentioned some aspects of new developments in the theory of tunneling in conjunction with variational transition state theory calculations.

The most significant qualitative points to emerge from recent work on tunneling in chemical reactions are: 1. The tunneling contributions are

usually larger than would be expected by most workers. 2. Reaction-path curvature effects are often very large, i.e., accurate transmission coefficients can be calculated only by using dominant tunneling paths systematically displaced from the minimum-energy reaction path. 3. Tunneling probabilities for multidimensional systems can nevertheless be calculated reliably in most or all cases by reduced-dimensionality semi-classical methods.

The simplest and most commonly used methods for approximating tunneling effects in conventional TST are the methods of Wigner (191) and Bell (10). In both these methods the potential along the minimum energy path in the vicinity of the saddlepoint is approximated as a truncated parabola. The transmission coefficient is obtained by Boltzmann-averaging the semiclassical barrier penetration probabilities. Wigner's tunneling correction is a semiclassical approximation to lowest order in h. This correction factor is valid only when the correction is small, typically less than a factor of 2. Bell's method has a larger region of validity but the expressions are discontinuous and contain divergences. Recently, Skodje & Truhlar (160) have presented a continuous, divergence-free analytic expression for the transmission coefficient for a truncated parabolic barrier that approximates the accurate uniform semiclassical transmission co-efficients over a wide range of parameters (see also 11). The method is also applicable to unsymmetric barriers and is shown to be useful for barriers with shapes other than parabolic. They also found that it is best to fit the barrier to a parabola using the effective parabolic width of the nonparabolic barrier at energies that contribute appreciably to the transmission coefficient.

The first successful approximation for tunneling in systems with significant reaction-path curvature was developed by Marcus & Coltrin (108) and extended by Garrett & Truhlar (54, 57, 60, 62). This method calculates the tunneling action integral along the caustic envelope of a family of unbound trajectories with quantized adiabatic vibrations; this is called the Marcus-Coltrin path (MCP). More recently, Gray and co-workers (76) developed a semiclassical adiabatic model using the reaction-path Hamiltonian (118) and treating the kinetic energy terms containing curvature coupling by second-order classical perturbation theory. They used this second-order (SO) tunneling method involving the adiabatic barrier to study the unimolecular isomerization of HNC to HCN (76) and the unimolecular decomposition of formaldehyde (77). Forst (52) also treated tunneling in formaldehyde decomposition; however, he used the classical barrier and neglected reaction-path curvature. Cerjan et al (25) unified the semiclassical perturbation approximation with the infinite order sudden approximation applied to the reaction-path Hamiltonian to obtain an expression for the total reaction probability that takes the form of a zero-

curvature adiabatic reaction probability times a curvature-dependent correction factor.

Skodje et al (162, 163) developed a semiclassical adiabatic model that is valid for systems with small reaction-path curvature, and they derived a criterion for the validity of the adiabatic approximation in curvilinear natural collision coordinates. The small-curvature (SC) tunneling method is similar to the collinear-reaction method of Marcus & Coltrin (108) but can be applied without singularities to systems with large reaction-path curvature, and it is expected to be more accurate for small-curvature systems. In addition it is applicable to noncollinear systems with reaction-path curvature components in more than one degree of freedom, for example it has been applied to calculate large tunneling corrections for the reactions $OH + H_2$ and isotopic analogs, which have curvature components in four of the five vibrational coordinates (84, 181). Skodje et al also compared, both formally and numerically, the MCP, SC, and SO tunneling methods, a previously suggested method [the phase average (PA) method (118)], and three new methods [the vibrational average (VA), the dynamical-path vibrational average (DA), and the semiclassical optical potential (SOP) methods]. These adiabatic methods may be classified into two general groups, depending upon the method used to remove from the kinetic energy term the dependence upon the coordinates of the bound degrees of freedom orthogonal to the reaction coordinate. One class of models (PA, SO, VA, DA, and SOP) accomplishes this by "averaging" the reaction-path Hamiltonian over the vibrational coordinates either classically or quantally. The other class (MCP and SC), which is systematically more successful, defines single values of the vibrational coordinates for each value along the reaction coordinate. These "vibrational-collapse" models have the physical interpretation that the tunneling is forced to occur along a specified path through the interaction region.

For reactions with large reaction-path curvature, the adiabatic approximation breaks down. Large reaction-path curvature occurs, for example, in systems in which a light atom is transferred between two heavy atoms or molecules. Babamov, Marcus, and Lopez (6–8) developed a method for computing the reaction probability for this type of system, and they applied it to study tunneling probabilities in the threshold region as well as the oscillations of the reaction probability as a function of energy for energies above threshold. Garrett, and co-workers (74) developed a similar method, which they called the large-curvature (LC) method, and they used it to calculate thermally averaged tunneling correction factors for VTST. The physical model for a collinear atom-diatom reaction is that the tunneling occurs by the most direct path (a straight line) connecting the reactant and product regions. Motion in the bound vibrational coordinate (rather than translational motion along the reaction coordinate) promotes

tunneling, and for a fixed total energy, tunneling can begin at a wide range of geometries along the caustic parallel to the reaction coordinate from the asymptotic reactant region to the turning point in the adiabatic potential. This method was demonstrated to work well for the Cl + HCl reaction and isotopic variants in both 1D (17) and 3D (74).

Garrett & Truhlar (65) unified the LC method with the vibrational-collapse adiabatic models by developing a least-action (LA) tunneling method. In this method the optimum tunneling path is chosen from a set of parameterized paths by requiring it to be the one that accumulates the least imaginary action along the tunneling path. This method was found to be extremely successful for a system with small-to-large reaction-path curvature. In practice, transmission coefficients based on the LC and LA approximations are based on the ground state and are called LCG and LAG, respectively. See (180) for formulas for applying these methods to general polyatomic systems.

The methods described above have been applied to reactions with barriers in the regions of large reaction-path curvature, and reaction-path curvature effects on tunneling probabilities have been found to be very important in many cases. For reactions with no barrier, or barriers far into the reactant and product regions, it is possible to simplify the treatment of reaction-path curvature. Illies, Jarrold, and Bowers (83, 87) proposed a tunneling model to describe the unimolecular fragmentation of CH_4^+ and NH_3^+, which are reactions with loose transition states. They approximated the potential in the tunneling region by a dipole term plus a rotational barrier from free internal rotation of the molecular fragments and orbital rotation. Using this model they obtained good agreement between calculated rate constants and experimental ones.

Heller & Brown (80) presented a method to estimate surface-hopping probabilities from a bound state on an upper surface to a bound state on a steep lower surface that does not cross (or avoids crossing) the upper surface in the classically allowed region, for the case in which a single path dominates the tunneling. Although the problem is formally quite different from the problem of single-surface reactive scattering for which the LA method was developed, the semiclassical solution has some points in common, especially with our small-curvature limit. Cross-fertilization of the two methods may provide clues as to how to extend both to a wider range of problems.

Transition state theory with tunneling has also been used to examine intramolecular hydrogen-transfer reactions. LeRoy (98) used a phenomeno-logical model to calculate the rate of transfer of hydrogen atoms between two nonequivalent sites in large polyatomic molecules. The physical model is that vibrational stretching of the bond being broken initiates the reaction, although it is not necessary that 100% of the energy in the vibration is

available for promoting the reaction. The effects of the degrees of freedom orthogonal to the reaction coordinate enter the rate expression through a steric factor. Adjusting the steric factor, the percentage of vibrational energy available to the reaction coordinate, and the effective one-dimensional potential along the tunneling path, LeRoy found he could reproduce experimental data for several intramolecular H atom transfer reactions. Bicerano et al (12) studied a similar problem, the transfer of a hydrogen atom between equivalent sites in malonaldehyde. For this symmetric system the potential along the minimum energy path between the two equilibrium geometries is a symmetric double well potential. Tunneling was included in the vibrationally adiabatic approximation with potential parameters taken from ab initio electronic structure calculations. Instead of calculating the rate of transfer from one well to another, they computed the effect of tunneling upon the energy level splitting, obtaining a result within a factor of two of the experimental one. The polyatomic VTST formalism discussed above can also be applied to multidimensional unimolecular isomerizations, with SC, LC, or LA tunneling corrections (180; F. B. Brown and D. G. Truhlar 1984, unpublished).

Vibrationally Adiabatic Barriers

The free energy of activation curve as a function of reaction coordinate reduces at 0 K to the vibrationally-rotationally adiabatic ground-state, s-wave potential curve, or, for short, the vibrationally adiabatic ground-state potential curve $V_a^G(s)$. When the shape of this curve is dominated by the s dependence of high-frequency modes, then the barriers of $V_a^G(s)$ provide a guide to the location of dynamical bottlenecks at nonzero temperature or nonzero microcanonical energy. Similarly, the barriers of vibrationally adiabatic excited-state curves may provide dynamical bottlenecks for reactions of vibrationally excited species.

Agmon (3) suggested using an alternative coordinate system to calculate $V_a^G(s)$, with the goal of improving the accuracy of the separability of the reaction coordinate that must be assumed in TST or VTST. A difficulty with Agmon's coordinate system is that the kinetic energy operator of the generalized transition state is complicated because the vibrational coordinates are curved. Reaction-path Hamiltonians based on the minimum-energy path and non-curved vibrational coordinates (56, 57, 70, 84, 104–107, 118) allow for more convenient calculations of the vibrational energies of the generalized transition states; yet, in a quadratic expansion about any point on the reaction path, the potential energy contains no cross-term coupling the reaction coordinate to the vibrational coordinates.

Pollak (130, 132–134) calculated vibrationally adiabatic potential curves and transmission probabilities for the vibrationally excited collinear $H + H_2$ reaction and isotopic analogs by quantizing pods, and also, in

Jacobi coordinates, by treating the one-dimensional bound vibrational motion quantum mechanically and the reaction-coordinate motion by a parabolically uniformized semiclassical approximation. He obtained qualitatively similar results to earlier state-selected vibrationally adiabatic calculations (57), but better agreement with accurate quantal results for reaction probabilities of vibrationally excited species. The earlier calculations had been carried out by the Morse I approximation applied to locally straight dividing surfaces in coordinates based on the minimum-energy reaction path. The quantitative differences were attributed to the Morse I approximation and to the neglect of important curvature corrections that are contained in pods. Garrett & Truhlar (1984, *J. Chem. Phys.* In press) have performed calculations employing straight-line dividing surfaces perpendicular to the minimum-energy path and using the WKB approximation for vibrational energies; the new calculations yield excellent agreement with adiabatic barrier heights obtained by quantizing pods and also with accurate quantal rate constants for the vibrationally excited case. This shows that curved generalized transition states are not necessary for high accuracy. As mentioned in a previous section, the Morse I approximation, which is very convenient, is usually adequate for thermal reactions, but WKB or quantal vibrational eigenvalues may be required for good accuracy for excited states.

Pollak (130, 132), Lee et al (96), and Ron et al (153) also used pods and vibrational energy calculations in Jacobi coordinates to evaluate adiabatic barriers for collinear and reduced-dimensionality calculations on the reactions $F + H_2$ and isotopic analogues and $O + H_2$. A disadvantage of Jacobi coordinates is that they yield accurate adiabatic barriers only relatively far out in the reactants and products channels; and a disadvantage of pods is that they exist only for collinear atom-diatom reactions. Methods based on minimum-energy reaction paths are more general, although they may be inappropriate in regions of very large reaction-path curvature; fortunately we have found in applications that this is not a problem because the variational transition state tends not to be located in such regions.

Garrett & Truhlar (57) and Pollak (132) also used adiabatic transmission probabilities to calculate the cumulative reaction probability, which has a step-like character due to channel openings; these steps should not be confused with oscillations in the state-selected reaction probabilities, which are due to interference effects such as resonances, but may sometimes be explained (46) by invoking only quantal discreteness.

The main reason that quantized VTST is more reliable than standard trajectory calculations for thermal rate constants is that it incorporates quantized energy requirements at dynamical bottlenecks, i.e. it incorporates the constraints of quantized adiabatic barriers. Schatz (154) suggested

incorporating such energy constraints for low-frequency, classically non-adiabatic bending modes as ad hoc additions to the potential energy surface for three-dimensional trajectory calculations.

State-selected Reactions

The discussion in the main part of this review is centered on thermal rate constants, which are the traditional domain for transition state theory. The methods of variational transition state theory and related methods are also useful for understanding excited-state reactivity in certain cases. For example, adiabatic barriers, as discussed above, may be used to interpret excited-state reactivity and product-state distributions (130, 133, 197). Full rate constant calculations for vibrationally excited species may also be performed by invoking the vibrationally adiabatic or diabatic approximation for one degree of freedom and variational transition state theory for others; such calculations have been performed for several collinear reactions (57, Garrett & Truhlar 1984, *J. Chem. Phys.* In press), for three-dimensional $H + H_2$ and $D + H_2$ (B. C. Garrett and D. G. Truhlar 1984, unpublished), and for three-dimensional $OH + H_2$ (179). For $OH + H_2$ ($n = 1$), conventional TST predicts a vibrational rate enhancement of $> 10^4$, whereas state-selected VTST predicts 10^2, which is in good agreement with experiment (75, 199). State-selected VTST calculations (179) for $OH + H_2$ also imply that the large-non-Arrhenius behavior for $OH + H_2$ is not a consequence of the rate enhancement for vibrationally excited H_2, as had been suggested (198).

Pollak & Pechukas (143) showed that one may map out the reactant and product classical vibrational energy distributions by studying trajectories initiated in the immediate vicinity of variational transition states.

Resonances

The vibrationally adiabatic potential curves of variational transition state theory are also very useful for predicting and classifying collisional resonances in many chemical reactions, especially for thermoneutral and nearly thermoneutral reactions for which reaction-path curvature is small or intermediate (9, 64, 71, 158, 159). Variational transition states provide the barriers to decay of the resonance in the one-dimensional vibrationally adiabatic model. For large reaction-path curvature or strongly exothermic reactions, approaches based on resonant periodic orbits or on adiabaticity in hyperspherical coordinates appear more useful [see, for example, (139, 144, 152) and references therein].

Vibrational Bonding

Vibrational bonding has received considerable attention in the last couple of years, and it is interesting to point out how, like resonance phenomena, it can often be predicted and understood in terms of the same concepts and

quantities as developed for variational transition state theory. In particular, vibrational bonding may be considered as the extreme of a pre-threshold resonance. For example, we observed pre-threshold resonances for collinear reactions with mass combinations $H + FH$ and $D + FD$ on a low-barrier potential energy surface, and these can be understood vibrationally adiabatically (71, 159). If the mass combination is changed to heavy-light-heavy, for which generalized-transition-state vibrational energy requirements show the most pronounced minimum in the interaction region (58), the vibrational energy of the resonance will decrease, and the resonance energy may drop below the zero point energy of the atom-diatom reactants and thus become a true bound state, even though the lowest point on the potential surface still occurs for the asymptotic atom-diatom reactants. This is called vibrational bonding, as opposed to ordinary bonding, with an equilibrium geometry corresponding to the minimum in the potential energy surface. A vibrational bonding state was first reported for collinear IHI (101), and shortly thereafter a vibrational bonding state for three-dimensional IHI was calculated (39, see also 101, 137). Variational transition states may serve as effective barriers that contribute to localizing a vibrational-bonding state in the strong interaction region. Adiabatic bonding is expected more generally in excited-state vibrationally adiabatic curves than in ground-state ones; if the adiabatically bound state in an excited-state vibrationally adiabatic potential curve lies below the asymptote, it may still decay nonadiabatically (158, 159), and thus the state is only quasibound. Only when vibrational effects are largest does one expect to find states below the asymptote of $V_a^G(s)$, and hence vibrational bonding will occur far less frequently than the similar resonance effect.

CONCLUDING REMARKS

In the last few years it has been shown that variational transition state theory can be implemented usefully for practical calculations of chemical reaction rates from potential energy surfaces. When combined with accurate semiclassical tunneling calculations, VTST is the most accurate practical method available for such calculations. Variational-transition-state constructs are also useful for quantitative interpretations of excited-state reactivity and resonances.

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