

we cannot properly identify the reaction coordinate; this raises particular problems for the treatment of kinetic-isotope effects. With all of these criticisms Eyring was in full agreement.

The second standpoint from which we must judge transition-state theory is: To what extent does it provide us with a conceptual framework with the aid of which experimental chemists (and others) can gain some insight into how chemical processes occur? On this score the theory must receive the highest marks; for nearly half a century it has been a valuable working tool for those who are not concerned with the calculation of absolute rates but are helped by gaining some insight into chemical and physical processes. The theory provides both a statistical-mechanical and a thermodynamic insight—one can take one's choice or use both formulations. It leads to extremely useful qualitative predictions, without the need

for any calculations, of solvent effects, relative rates of similar processes, kinetic-isotope ratios, pressure influences, and a host of other important effects.

Porter's assessment in 1962<sup>90</sup> of transition-state theory makes the point very well: "On the credit side, transition-state theory has an indestructible argument in its favour. Since its inception, it has provided the basis of chemical kinetic theory; imperfect as it may be, it is undoubtedly the most useful theory that we possess. During the last twenty-five years its greatest success has been not in the accurate prediction of the rates even of the simplest reactions, but in providing a framework in terms of which even the most complicated reactions can be better understood". Most of us would agree that these comments remain valid today.

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(90) G. Porter, ref 86, p 2.

## Current Status of Transition-State Theory

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We review the current status of transition-state theory. We focus on the validity of its basic assumptions and of corrections to and improvements of conventional transition-state theory. The review is divided into sections concerned in turn with bimolecular reactions in the gas phase, unimolecular reactions in the gas phase, and isomerizations and atom-transfer reactions in liquid-phase solutions. Some aspects that are emphasized are variational transition-state theory, tunneling, the assumption of an equilibrium distribution of reactants, and the frictional effects of solvent molecules.

### 1. Introduction

Transition-state theory has achieved widespread acceptance as a tool for the interpretation of chemical reaction rates. The theory has, however, been less successful in its original goal, the calculation of absolute reaction rates. A difficulty with the calculation of absolute reaction rates is that it requires very accurate knowledge of potential energy surfaces. For example, an error of 1 kcal/mol in an activation barrier causes an error of a factor of 5.6 in a rate calculation at room temperature, and an error of 2 kcal/mol causes an error of a factor of 31. Even though very remarkable advances have been made in the calculation of potential energy surfaces, it is still very hard to calculate activation barriers this accurately even for

simple reactions. Furthermore, it may be necessary in many cases to calculate global regions of the potential surface, not just barrier heights, in order, for example, to accurately treat systems with large tunneling effects or systems with temperature-dependent or energy-dependent dynamical bottlenecks.

Despite the difficulties, many workers remain enthusiastic about the value of absolute rate calculations for a variety of reasons. First of all, the methods of electronic structure theory and the capabilities of computers are still improving rapidly. Accurate ab initio prediction of activation barriers for simple reactions and then for increasingly complicated ones may be "just around the corner". However, when ab initio methods are still insufficiently

accurate, there is always hope for empirical or semi-empirical correlations, especially when these are carried out in the convenient transition-state-theory formalism of enthalpy of activation, entropy of activation, and heat capacity of activation.<sup>1</sup> Furthermore, in some applications, as for kinetic isotope effects and high-temperature rate constants, the sensitivity of the calculated results to the barrier height of the potential energy surface is reduced. For other cases, as in choosing between postulated mechanisms for some reactions of complicated species, definite conclusions can be drawn even in the face of large uncertainties in the absolute rate constants. In still other cases, e.g., reactions of mechanistic intermediates or reactions under extreme conditions, there may not be a good way to obtain information on rate coefficients by laboratory experiments, so theory may be the *only* recourse. Thus, absolute rate calculations can often be very useful, and we may expect them to become more and more useful as techniques for both the structural and dynamic parts of the calculation improve. Transition-state theory, despite its age, is still the method of choice for most attempts at absolute rate calculations. Furthermore, it appears to be almost without competition for more qualitative discussions of a wide variety of important questions in chemical kinetics, such as solvent effects. The reduction of the dynamics problem to the consideration of a single structure provides unique opportunities for qualitative considerations; e.g., can this fast a rate constant or these relative rates possibly be consistent with this transition-state structure?

As discussed very clearly in the preceding article by Laidler and King,<sup>2</sup> the calculation of absolute reaction rates from potential energy surfaces was cast in a particularly appealing form by Eyring in 1935.<sup>3</sup> Because of the simplicity and elegance of the resulting equations, they became widely used and are still widely used in their original 1935 form. Transition-state theory is based on a quasiequilibrium hypothesis with a simple physical interpretation. Most importantly from a practical standpoint, this quasiequilibrium hypothesis greatly reduces the computational requirements of the theory. The reduced computational requirements plus the ability of the theory to explain general trends in preexponential factors and kinetic isotope effects for bimolecular reactions and the energy dependence of rate constants for unimolecular reactions have been the major reasons for its general popularity.

Modern work, however, is not so constrained by the requirement to minimize computing, and a major goal of much current research on transition-state theory is to refine and improve or correct the theory, even at increased computational expense. This is the general goal of the rapidly widening field of generalized transition-state theories. Most attempts to improve the theory are based on incorporating more detailed dynamics into it. Concomitantly there is an effort to test transition-state theory, in both its conventional and generalized formulations, against more accurate dynamical theories and against experiment. The improved understanding of the dynamic basis of transition-state theory, the new developments in generalized transition-state theory, progress in learning how to make applications to complicated solution phenomena more realistic, and the successes, failures, and ambiguities

of the various tests constitute the current status of transition-state theory in physical chemistry, and these are the areas with which the present article is concerned.

Transition-state concepts are so widely used in chemistry that complete coverage of all current approaches and applications in one article seems impossible. This fact itself may be the greatest tribute to the theory and its founders. Recent extensions of the theory exhibit very encouraging vitality, however, so we expect that future successes of transition-state theory and closely related models descended from it will continue to make the task of complete coverage harder and harder and make our debt to the early work described in the preceding paper even greater. Having stated up front that it is impossible to be complete, we hope there will not be any misimpressions in this regard, and we will spend the rest of this article summarizing a few aspects of the current status of transition-state theory that are relevant to the general applicability of the theory. We will give representative examples rather than exhaustive references.

Before starting on the present review we wish to single out three recent reviews of transition-state theory by Pechukas.<sup>4-6</sup> All are very well written and are recommended strongly to anybody interested in the subject of the present review.

## 2. Dynamical Foundations and Key Concepts

A good reference to mark the beginning of the modern era of transition-state theory is the classic paper of Eliason and Hirschfelder.<sup>7</sup> They formulated the equilibrium rate constant in terms of a Maxwell-Boltzmann average over state-to-state reaction cross sections, and in a very stimulating appendix they considered more rigorously than had been done previously how one may make a series of approximations leading to transition-state theory. They considered state-dependent transition states and proposed the idea of locating a generalized transition state to maximize the free energy of activation. Later Marcus<sup>8</sup> was to utilize the idea of state-dependent transition states very fruitfully, and Laidler and co-workers<sup>9</sup> and Szwarc<sup>10</sup> further developed the idea of maximizing the free energy of activation. These ideas form the basis, respectively, of the adiabatic theory of reactions<sup>11,12</sup> and canonical variational theory,<sup>12</sup> two important approaches in current work on generalized transition-state theory. Reexpression of the equilibrium rate constant as a thermal average of reaction cross sections plays an essential role in the use of modern collision theory<sup>13,14</sup> to calculate rate constants without the assumptions of transition-state theory, and thereby to

(1) S. W. Benson, "Thermochemical Kinetics", 2nd ed., Wiley, New York, 1976.

(2) K. J. Laidler and M. C. King, *J. Phys. Chem.*, preceding paper in this issue.

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(5) P. Pechukas, *Annu. Rev. Phys. Chem.*, **32**, 159 (1981).

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(7) M. A. Eliason and J. O. Hirschfelder, *J. Chem. Phys.*, **30**, 1426 (1959).

(8) R. A. Marcus, *J. Chem. Phys.*, **45**, 2139, 2630 (1966); R. A. Marcus in "Investigation of Rates and Mechanisms of Reactions", Part I, 3rd ed., E. J. Lewis, Ed., Wiley-Interscience, New York, 1974, p 13.

(9) C. Steel and K. J. Laidler, *J. Chem. Phys.*, **34**, 1827 (1961); K. J. Laidler and J. C. Polanyi, *Prog. React. Kinet.*, **3**, 1 (1965); K. J. Laidler, "Theories of Chemical Kinetics", McGraw-Hill, New York, 1969; A. Tweedale and K. J. Laidler, *J. Chem. Phys.*, **53**, 2045 (1970).

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(11) D. G. Truhlar, *J. Chem. Phys.*, **53**, 2041 (1970). See also D. G. Truhlar and R. E. Wyatt, *Annu. Rev. Phys. Chem.*, **27**, 1 (1976).

(12) B. C. Garrett and D. G. Truhlar, *J. Phys. Chem.*, **83**, 1052, 1079, 3085(E) (1979); **84**, 682(E) (1980).

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check and improve the transition-state theory. A major assumption which must be made for practical applications of either transition-state theory or the Eliason-Hirschfelder formulation in terms of cross sections is that the observed rate constant may be approximated by the equilibrium one, or more precisely, the local-equilibrium one, which is the rate constant when reactant internal states are in equilibrium with each other and products are missing. (This assumption is necessary but not sufficient for the validity of transition-state theory.)

The variational approach to transition-state theory was formalized by Keck,<sup>15</sup> following up on early work of Wigner<sup>16</sup> and Horiuti,<sup>17</sup> in a paper and a review that laid a detailed classical mechanical foundation for much current activity. A prerequisite to the variational theory is the recognition of the conventional transition state as a configuration-space surface (actually hypersurface) obtained by deleting nonbound normal coordinates from a coordinate space centered at a saddle point on a potential energy surface. Then the fundamental assumption of transition-state theory is that the one-way equilibrium flux coefficient through the transition-state surface equals the equilibrium rate constant, which would be true if trajectories that pass through the surface never return. Keck's review points out that, if the transition state is generalized to be an arbitrary surface in phase space dividing reactants from products and depending on both coordinates and momenta, then it can be varied in such a way that the one-way equilibrium flux coefficient through the dividing surface does equal the equilibrium rate constant. The transition-state assumption would be exact for such a dividing surface. Important practical corollaries are that in classical mechanics the equilibrium one-way flux coefficient through any possible dividing surface provides an upper bound on the equilibrium rate constant, and the "best" generalized transition-state dividing surface may be found by varying the surface to minimize the calculated rate constant. This is variational transition-state theory.

The point of view used in the work of Wigner, Horiuti, and Keck that the transition-state-theory rate constant is the one-way equilibrium flux coefficient through a phase-space surface dividing reactants from products provides a collisional alternative to the quasiequilibrium viewpoint by which the transition-state-theory rate constant is the rate constant for conversion of an equilibrium concentration of transition states to products. The collisional viewpoint is more useful for incorporating dynamical corrections; the quasiequilibrium viewpoint is more useful for correlating reaction rates in terms of structural effects and activation parameters. In the quasiequilibrium formulation, the emphasis is on the equilibrium distribution in the dividing surface and the statistical character of the equilibrium approximation. In the collisional formulation the emphasis is on the dynamics that leads to the flux through the dividing surface. Although the quasiequilibrium approach, as emphasized, for example, in Eyring's formulation,<sup>3</sup> has been responsible for most of the popular usefulness of transition-state theory, the collisional or dynamical approach, as stressed, for example, in Wigner's early discussion,<sup>18</sup> is utilized in much of the current work directed to improving transition-state theory.

The collisional approach leads naturally to a focus on the transmission coefficient or conversion coefficient of

transition states to products.<sup>19</sup> Keck<sup>20</sup> and Anderson<sup>21</sup> used the collisional approach to elucidate the connection between transition-state theory and modern trajectory calculations. In particular they showed how trajectory calculations can be used to calculate a correction for the breakdown of the transition-state assumption when the transition state is located at a convenient place rather than completely optimized in phase space. Furthermore, they showed how the transition-state concept can be used to greatly reduce the computational effort required to do computer trajectory simulations of gas-phase rate processes with small rate constants. This idea has been extended to solid-phase and liquid-phase simulations by Bennett, Chandler, Berne, McCammon, Karplus, and co-workers,<sup>22-26</sup> and it is sure to be more and more influential as the complexity of systems that can be simulated continues to be increased.<sup>27</sup>

Detailed tests of transition-state-theory predictions against more accurate, or presumably more accurate, dynamical calculations have played a very significant role in defining the current status of transition-state theory, and this is expected to continue. This activity originated with Bunker's numerical tests of classical transition-state theory for unimolecular reactions against accurate classical trajectories<sup>28,29</sup> and with comparisons of quasiclassical and classical trajectory calculations to transition-state theory for bimolecular reactions by Karplus and co-workers.<sup>30</sup> These studies were soon followed by the first tests of transition-state theory against accurate quantum dynamical calculations for collinear collisions with bend corrections,<sup>31</sup> for pure collinear collisions,<sup>32</sup> and for three-dimensional collisions.<sup>33</sup> One result of these tests of transition-state theory against quantum dynamics was the conclusion that existing methods of incorporating quantal effects on reaction-coordinate motion in transition-state-

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theory transmission coefficients were inadequate.<sup>32</sup> This was attributed<sup>32,34</sup> to nonseparable effects, such as a negative internal centrifugal effect<sup>35</sup> caused by the curvature of the reaction path in mass-scaled coordinates. We will return to this point in discussing the current status of tunneling corrections in section 3.

A renaissance of interest in the classical foundations of transition-state theory was initiated by the paper of Pechukas and McLafferty<sup>36</sup> in 1973. They pointed out the conditions such that in classical mechanics transition-state theory is exact at threshold and for a finite energy interval above threshold, and their discussion utilized the collisional formulation of transition-state theory rather than the more popular quasiequilibrium formulation. Pechukas, Pollak, and others<sup>4-6,37,38a</sup> have continued to investigate the analytic mechanics of classical mechanical transition-state theory for collinear atom-diatom reactions, leading to many new insights into how the validity of the transition-state approximation is related to the nature of the classical trajectories for a given system. They have also suggested some new approximations to the rate constant, and they have discussed the relationship of transition-state theory to information theory, to the reactivity-selectivity principle, and to excited-state reactivity. Perhaps the most intriguing part of this work is the "pods", or periodic-orbit dividing surface. For collinear atom-diatom reactions, the best transition state, which in general is a hypersurface, becomes a curve in coordinate space, and this curve is given by a periodic trajectory. The flux through a pods is proportional to the action integral along the pods; pods with the same action as reactants are adiabatic barriers, and this has a special meaning for transition-state theory since the adiabatic theory of reactions is mathematically equivalent<sup>12</sup> to microcanonical variational transition-state theory for a one-parameter sequence of generalized transition-state dividing surfaces parametrized by their distance along a reaction coordinate. By quantizing pods, one obtains approximate adiabatic barrier heights for quantal reactions. Pollak and Wyatt<sup>38b</sup> have applied the collinear pods concept to three-dimensional atom-diatom reactions with a separation of time scales by means of an adiabatic reduction scheme; for such systems this provides a convenient alternative to quantizing the invariant manifold of higher-dimensional trajectories that forms the general multidimensional-reaction analogue of a pods.

Several purely mathematical tests of classical transition-state-theory and generalized transition-state-theory predictions for bimolecular reactions against accurate classical dynamical equilibrium rate constants have also been reported, for both collinear<sup>12,37,38a,39-42</sup> and three-di-

mensional<sup>43,44</sup> examples. As an example of the results obtained in these studies, consider the reaction probabilities calculated for a three-body collinear model of  $C_4H_9 + H-C_2H_5 \rightarrow C_4H_{10} + C_2H_5$  with a classical barrier height of 4.5 kcal/mol.<sup>40</sup> For this reaction conventional transition-state theory predicts reaction probabilities that agree with accurate classical dynamics up to 0.1 kcal/mol above the barrier. At higher energies the conventional theory fails badly and it overestimates the thermal rate constant by factors of 4.3 and 15 at 300 and 4000 K, respectively. In contrast, microcanonical optimization of straight-line dividing surfaces gives excellent agreement with the accurate classical reaction probabilities up to 0.2 kcal/mol above the barrier, and reasonably good agreement up to 1.5 kcal/mol above the barrier; this reduces the errors in the thermally averaged rates at the two temperatures mentioned above to factors of 1.3 and 2.0, respectively. For other collinear reactions that have been studied the agreement of transition-state theory with accurate classical dynamical results is better. At 300 K the typical error is 10% or less. At 2400 K the typical error is a factor of 2-3 for the conventional theory and 1.5-2 for microcanonical variational theory.

In classical mechanics, transition-state theory would provide exact equilibrium rate constants except for trajectories that recross the dividing surface through the saddle point, and variational transition-state theory would be exact except for trajectories that recross the variational dividing surface; the numerical tests mentioned in the previous paragraph show that such recrossing effects are strong functions of masses and potential energy surface, but generally become more important as the energy or temperature is raised. The numerical studies complement the analytic work discussed above in providing insight into the fundamental dynamical basis of transition-state theory. It has been pointed out<sup>45,46</sup> though that the quantitative validity of transition-state theory may be quite different in classical and quantum mechanics because threshold energies for bimolecular reactions in a quantum-mechanical world tend to be considerably higher than threshold energies for purely classical systems. This is so because reactant zero-point requirements are partially preserved in nonreactive modes at the dynamical bottlenecks. This has a significant quantitative effect on the reaction rate and may even put the system in a new dynamical regime, so that for a given reaction the validity of classical transition-state theory near the classical threshold may be quite different from the validity of quantized versions of transition-state theory near the quantal threshold. Although unimolecular dissociation reactions have a higher energy

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content and a high reactant density of states at threshold, classical considerations are not necessarily adequate in that case either.<sup>47,48</sup>

Modern unimolecular transition-state theory<sup>49-58</sup> has its roots in the Rice-Ramsperger-Kassel theory of unimolecular reactions, which assumes that the unimolecular rate constant is a function only of the total energy and, thus, does not depend on the manner in which the molecule is excited. A dynamical rationale for this is the assumption that the phase space of the dissociating molecule is chaotic and metrically indecomposable.<sup>28,29,59-63</sup> A very active area of current work is the analysis of chaotic classical behavior of Hamiltonian systems to determine whether classical ergodicity provides a mathematical basis for the energy randomization assumption of unimolecular rate theory.<sup>61-63</sup> A particularly vexing and still unsettled question concerns the relation of classical and quantal ergodicity and in fact there is much controversy even about the meaning of quantum chaos.<sup>63</sup>

In Rice-Ramsperger-Kassel theory, vibrations within the molecule are represented as  $s$  strongly coupled harmonic oscillators freely exchanging energy. The microcanonical rate constant  $k(E)$  for total energy  $E$  is taken as the statistical probability that a particular oscillator has energy in excess of the unimolecular threshold  $E_0$ ; the well-known result for the rate constant is  $A[(E - E_0)/E]^{s-1}$ . The concept of a transition state is not required in deriving this expression. The present form of the statistical theory of unimolecular reactions was derived in the early 1950s by assuming a quasiequilibrium between the energized molecule and a transition state<sup>64-66</sup> and is generally known as the Rice-Ramsperger-Kassel-Marcus (RRKM) theory. It is sometimes called the quasiequilibrium theory (QET),<sup>67</sup> especially for applications to unimolecular decomposition of excited ions to predict mass spectral patterns.

In dynamical formulations the basic assumptions used to derive RRKM theory are (i) the Rice-Ramsperger-Kassel assumption that all molecular states of a given total energy are equally accessible (uniform density in reactant

phase space) and will ultimately lead to products and (ii) the transition-state assumption that dissociating trajectories corresponding to these states do not recross a phase-space surface dividing reactants from products. This surface is the transition state or "critical configuration".<sup>29,68</sup> The result of RRKM theory is a microcanonical rate constant  $k(E, J)$  that depends on the total angular momentum  $J$  as well as the energy and is given by the sum of states for the transition state divided by the density of states for the reactant. For classical mechanics, harmonic oscillators, and  $J = 0$ , the RRKM rate expression reduces to the Rice-Ramsperger-Kassel one, where  $A$  is identified as the product of the  $s$  reactant vibrational frequencies divided by the product of the  $s - 1$  transition-state vibrational frequencies. The advantage of the transition-state reformulation of the theory is that it allows for realistic comparisons with experimental results by using quantal sums and densities of states based on frequencies taken from potential energy surfaces or transition-state models. The use of accurate or reasonable semiclassical expressions for the sums and densities of states is important for qualitatively correct predictions,<sup>51,52,69</sup> and the use of efficient and accurate semiempirical expressions<sup>70,71</sup> for these quantities was instrumental for widespread applications of the theory.

In many applications and presentations of RRKM theory it is assumed that the transition state is located at the saddle point on the potential energy surface. The unimolecular threshold, without tunneling, is taken as the classical potential energy barrier plus the zero-point energy difference between the transition state and reactant molecule. Bunker and Pattengill<sup>68</sup> attempted to make the transition-state structure consistent with the underlying assumption that it represents a dividing surface between reactant and products. They determined microcanonical unimolecular rate constants for dissociation of triatomic molecules from classical trajectory calculations. In their work, the dividing surface (critical configuration) was located by finding the smallest value of the reaction coordinate for which, once attained, the trajectory dissociated to products and did not return to the reactant region of phase space. When critical configurations chosen in this manner were used, nearly exact agreement was found between RRKM and trajectory rate constants. The critical configuration found by the dynamical criterion of Bunker and Pattengill was significantly tighter than the structure at the centrifugal barrier. This finding explained<sup>54</sup> the tight critical configuration structures required to fit alkane dissociation experimental rate constants with RRKM theory.<sup>72</sup> Bunker and Pattengill<sup>68</sup> found that the critical configuration derived from the trajectory calculations could be fitted by minimizing along the reaction coordinate the convolution of the density of internal states and the translational density of states and they proposed this as a variational approach for choosing the critical configuration. Although the correct microcanonical variational criterion is now recognized to be the minimization of the

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sum of states along the reaction coordinate,<sup>57,73-75</sup> in many cases the difference in the results of the two criteria is insignificant,<sup>74-76</sup> and the work of Bunker and Pattengill does illustrate that variational concepts similar to those of Wigner, Horiuti, and Keck for bimolecular reactions are also important in unimolecular rate theory.

To derive an expression for the thermal unimolecular rate constant like that for the Lindemann mechanism an additional postulate concerning intermolecular collisions must be made.<sup>49-54</sup> The most common postulate, called the strong-collision assumption, is that large enough amounts of energy are transferred in molecular collisions so that deactivation and activation may be viewed as single-step processes, in contrast to ladder-climbing processes. If the collisions are random and, thus, uncorrelated, the probability that an energized molecule avoids a collision for time  $\tau$  is  $\exp(-\omega_{\text{col}}\tau)$ , where  $\omega_{\text{col}}$  is the collision frequency. As discussed in many places<sup>29,59,60,64</sup> this distribution and that of random lifetimes give the RRKM result. The thermal unimolecular rate constant is the Boltzmann average of  $\omega_{\text{col}}k(E,J)/[\omega_{\text{col}} + k(E,J)]$ . At high pressures, so that  $\omega_{\text{col}} \gg k(E,J)$  this becomes the QET or transition-state-theory expression for the unimolecular rate constant. For ultrahigh pressures and in a condensed medium where collisional events become correlated, RRKM theory is no longer applicable, and a quasidiffusion theory becomes necessary.<sup>53</sup> An active area of current research is the development of a transition-state-type theory which is appropriate for condensed phases and is also extendable to problems of interest to gas-phase unimolecular kineticists.<sup>77,78</sup>

Most modern investigations of the validity of transition-state theory in solution owe a debt to and are, or ought to be, couched in terms of the seminal work of Kramers expounded in a classic 1940 paper.<sup>79</sup> Kramers viewed a reaction as a barrier passage influenced by interaction with the surrounding solvent molecules. The latter influence was described in simple Brownian motion terms via the stochastic Langevin equation. That is, the dynamical influence of the solvent was accounted for by a damping force, proportional both to the velocity along the reaction coordinate and to a friction constant  $\zeta$ . The friction constant  $\zeta$  is not very clearly identified by Kramers theory, but it is expected to increase with solvent density, pressure, and viscosity. Kramers identified several key regimes. (i) In the first of these, collisions with the solvent molecules are sufficient to maintain an energy equilibrium distribution for the barrier passage but are not so frequent as to disturb the free passage over the barrier; i.e., there is negligible solvent-induced recrossing. This is the regime where, in the absence of intrinsic recrossing effects such as might occur even in dilute gases, transition-state theory is valid, i.e., where the equilibrium conditions assumed in the standard formulation<sup>3</sup> are satisfied. (ii) In the second regime, collisions with solvent molecules lead to a recrossing of the barrier top before a stable product can be formed. This reduces the rate below the transition-state-theory prediction to a degree dependent on the solvent friction. An extreme limit of this can be reached for broad, flat barriers and high friction. There, collisions

are so frequent and effective that there is considerable barrier recrossing, and the reaction is a diffusion-controlled passage over the barrier. The rate becomes inversely proportional to friction, and it may be an order of magnitude or more below the transition-state-theory value. This is called the friction-limited regime. (iii) At low friction another source of breakdown of transition-state theory was identified by Kramers. Here the reacting system is weakly coupled to the solvent, and an equilibrium distribution in energy cannot be maintained. This is the same phenomenon as is responsible for falloff behavior in gas-phase unimolecular reactions (section 4), and, in the extreme case, the rate of reactant activation or product deactivation by energy transfer becomes rate limiting. Kramers found that, in this regime, the rate is far below the transition-state-theory value and is proportional to the solvent friction. This will be called the energy-transfer-limited regime. The energy-transfer-limited and friction-limited regimes are sometimes called the underdamped and overdamped cases, respectively,<sup>80</sup> or the weak-bath-coupling and strong-bath-coupling regimes.

Another key concept in the application of statistical mechanics to reaction rates in solution is the equilibrium time correlation function, which is free from the assumptions both of transition-state theory and of solvent specifics. In a landmark paper,<sup>81</sup> Yamamoto expressed the rate constant in terms of a time correlation function and showed that for equilibrium reactants in the gas phase this could be reduced to a reactive cross section form of the type discussed by Eliason and Hirschfelder.<sup>7</sup> An advantage of the time correlation function approach lies in the fact that the formula holds independent of phase. In particular, it applies in solution, when the notion of collisional cross section is at best murky and often completely inapplicable. In contrast the time correlation function is the basis for practical calculations on solution reactions by both numerical and analytic approaches; for example, the correlation function approach has been developed into a practical method whereby classical rate constants can be determined in condensed-phase systems using a trajectory simulation method with sampling at the transition state (as discussed in section 5). The time correlation function approach is related to transition-state theory as follows.<sup>23,78,82</sup> The observable rate constant may be written as the long-time limit of the net flux coefficient across a dividing surface as used originally in gas-phase studies,<sup>4,15,36,83</sup> or it may be written as the time integral of the time correlation function of the flux across a surface dividing reactants from products. If the dividing surface is chosen as a barrier top, then the initial-time value of the classical flux time correlation function is the classical transition-state-theory rate constant multiplied by a delta function in time. This corresponds to a singular initial contribution of "free streaming" trajectories crossing the dividing surface from the side of reactants to the side of products. The time integral of this contribution is  $k^{\text{TST}}$  itself. Any subsequent recrossing of the dividing surface induced by interaction with the solvent will lead to a negative tail in the flux time correlation function vs. time. This decreases the time integral and so reduces the rate constant below its transition-state-theory value. A convenient way to quantify this is via the ratio of the phenomenological rate to its transition-state-theory value.

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This defines a dynamical transmission coefficient. Thus, any effects of solvent dynamics on the rate leading to deviations from transition-state theory show up very clearly in the time correlation function formalism.

In most discussions of kinetics in solution the concept of a solvent cage plays a prominent role. The cage effect shows up two ways. First, for fast bimolecular reactions and high friction, the process of diffusional approach or separation of reagents, i.e., cage-to-cage jumping, may become the rate-limiting elementary step in a mechanism. Transition-state theory has sometimes been applied to the physical diffusion process, but the present article is concerned with applications of transition-state-theory concepts to more chemical elementary steps, such as atom transfer, unimolecular decompositions and rearrangements, and conformational isomerizations. The second effect of solvent cages is the interaction of the inner solvation shell with the primary chemical species during the reactive event. This effect is considered here using the language of friction. When frictional effects are large enough, the primary reaction step becomes diffusional on a vibrational length scale; this should not be confused with the process mentioned above of longer-range spatial approach or separation of reagents.

In the subsequent sections we briefly consider the current status of transition-state theory for gas-phase bimolecular reactions in a quantum-mechanical world, for unimolecular reactions, and for condensed-phase reactions.

### 3. Gas-Phase Bimolecular Reactions

*Quantized Theory for Bimolecular Reactions.* A paper that stimulated a great amount of interest and further activity was Miller's formulation<sup>83</sup> in 1974 of a semiclassical transition-state theory as an approximation to the exact expression for the equilibrium rate constant in terms of scattering matrices. Miller and co-workers followed this with a series of papers<sup>84</sup> presenting alternative semiclassical formulations and some numerical applications. These methods have not received widespread use but the papers are a gold mine of ideas, and they will probably continue to influence new developments for a long time. The fundamental problem with achieving a quantum-mechanical transition-state theory is that the one-way equilibrium flux across a dividing surface is a classical concept, and any attempt to translate it into quantum mechanics runs into the ambiguity of noncommuting operators. This also leads to a plethora of choices for semiclassical approaches. A succinct review of Miller and co-workers' work on semiclassical approximations has been given by Pechukas.<sup>5</sup>

McLafferty, Pechukas, and Pollak have also worked on the subject of a quantum transition-state theory, with the goal of establishing a quantal upper bound analogous to the rigorous variational theory of classical mechanics.<sup>4,85,86</sup>

The current status and future prognosis appears to be that a useful and accurate quantal upper bound is unattainable.

The conventional way to quantize transition-state theory is that used by Eyring<sup>3,67,87</sup> and followed in standard references:<sup>50,88-91</sup> one simply replaces the classical partition

functions by quantized ones. This corresponds to quantizing the system in the transition-state dividing surface, which is unstable, as if it were a stable system. Then, quantal effects on reaction-coordinate motion, which is orthogonal to the transition-state dividing surface, are included in a multiplicative transmission coefficient, which in principle may also include corrections for systems classically recrossing the transition-state dividing surface (as discussed in section 2) and/or corrections for nonequilibrium distributions in the reactants. This procedure has been applied to generalized transition states and has been used as the basis for an approximate variational transition-state theory for applications in a quantum-mechanical world.<sup>12,45,46,92-97</sup> Garrett and Truhlar<sup>12,92,93</sup> defined a single-parameter sequence of generalized transition-state dividing surfaces that are locally orthogonal to a reaction path, which is usually taken as the junction of the paths of steepest descent<sup>98</sup> through mass-scaled coordinates from the saddle point to reactants and products. (The scaling is proportional to the square root of the mass so that the kinetic energy becomes a diagonal quadratic form with the same reduced mass for all coordinates. The path of steepest descent through mass-scaled coordinates is called the intrinsic reaction coordinate, and it has the interpretation that it is the classical trajectory followed by an infinitely damped system starting at the saddle point.<sup>99,100</sup>) Each generalized transition state in the sequence is quantized by the conventional prescription, and the rate constant is minimized for a canonical ensemble or a microcanonical ensemble, leading to canonical variational theory (maximum-free-energy-of-activation method) or microcanonical variational theory. A transmission coefficient is included after the variation to account for quantal tunneling and nonclassical reflection in the reaction-coordinate motion. An improved canonical variational theory that treats the threshold energy by microcanonical variational theory and above-threshold contributions in terms of a truncated canonical ensemble has also been developed.<sup>94</sup>

Both conventional transition-state theory and the variational theories discussed in the previous paragraph have been tested against accurate quantum-mechanical results for 30 cases of collinear atom-diatom reactions (26 reactions and isotopic analogues on 12 potential energy surfaces), and they have been tested against presumably accurate quantal results for the  $H + H_2 \rightarrow H_2 + H$ ,  $H + BrH \rightarrow HBr + H$ , and  $H + BrD \rightarrow HBr + D$  reactions on approximate potential energy surfaces in three dimensions.<sup>12,94,96,101-105</sup> In general, the agreement between the

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rate constants calculated by variational transition-state theory with consistent transmission coefficients and the accurate quantal rate constants is very good. For the 33 cases considered, the ratio of the conventional transition-state-theory rate constant with unit transmission coefficient to the accurate quantal one at 300 K ranges from 0.44 to  $3.0 \times 10^3$ , and it is within the ranges 0.50–2.0, 0.40–2.5, and 0.20–5.0 in only 8, 14, and 23 cases, respectively. In contrast, this ratio for canonical variational theory with transmission coefficients computed by methods discussed below ranges from 0.57 to 1.54 in all cases. With classical reaction-coordinate motion for both theories, the ratio of the conventional transition-state-theory rate constant to the canonical variational theory one at 300 K is greater than a factor of 1.6 in 12 cases and is greater than a factor of 2.0 or 10 in 9 and 6 cases, respectively. Thus, variational optimization is very important, but so is tunneling, with an average transmission coefficient of 3.9 for the canonical variational theory calculations at 300 K. Note that 23 of the 33 test cases involve transfer of a hydrogen atom or one of its isotopes, and the other 10 also involve H or one of its isotopes in bond making or bond breaking; tunneling would be expected to be less important if no hydrogens are involved at the reaction center. Next we discuss the physical effects responsible for the location of the variational transition state and the methods<sup>106,107</sup> used for the transmission coefficients.

**Variational Corrections.** Garrett and Truhlar have given several discussions of the important factors determining the size of the variational corrections to conventional transition-state theory.<sup>12,45,46,92,108,109</sup> Usually the microcanonical and canonical variational criteria give similar results, so we need not make the distinction in this discussion. The variational transition state is located away from the saddle point when the generalized free energy of activation is not a maximum there. For a unit transmission coefficient, the generalized free energy of activation has a classical part, the Born–Oppenheimer potential along the reaction path, and a quantal part, the vibrational and rotational contributions. Since the saddle point maximizes the classical contribution, large variational corrections may be obtained only when the quantal contribution is significantly greater somewhere else, due to vibrational zero-point energies or entropic effects. A useful classification of systems is by the curvature of the reaction path through mass-scaled coordinates. When this is large, mass-scaled vibrational wells may widen, and zero-point energies may drop suddenly. If this occurs near the saddle point, variational corrections may be large. A constraint on reaction-path curvature is provided by the skew angle, defined as the angle in mass-scaled coordinates between the reactant and product valley floors. Small skew angles are associated with the transfer of a light atom or group

between two heavy moieties, and they require the reaction path to have large curvature. Large skew angles are associated with the transfer of a heavy atom or group between light moieties; in such cases reaction-path curvature is generally smaller. Variational corrections dominated by zero-point effects may be 1 or more orders of magnitude at room temperature, and they decrease with temperature. Such large effects are most likely to be found for small-skew-angle systems where the saddle point is in a region of large reaction-path curvature.<sup>46,92</sup> Variational corrections associated with entropic effects increase with temperature; an example is the tightening of an incipient bending vibration as a system passes an early saddle point. This bend effect tends to be a factor of 2–3 or less.<sup>46,92</sup> The systematics of whether the nontunneling variational transition-state-theory rate constant will differ from the conventional transition-state-theory one and of the temperature dependence of the location of the variational transition state have been explored for a series of atom–diatom reactions with model and semiempirical potential energy surfaces.<sup>46,92,109</sup> Consistent with the discussions above, symmetric-barrier reactions with large reaction-path curvature tend to show the largest variational corrections, which are dominated by stretching vibrations and decrease with temperature. Very asymmetric reactions show differences that increase with temperature and are dominated by bends. The results for atom–diatom reactions may provide a useful guide for variational corrections in larger systems. Two examples are provided in later paragraphs.

In reactions without saddle points the variational criteria become essential for the application of transition-state theory. Chesnavich, Su, and Bowers have applied classical variational transition-state theory to ion–molecule reactions with nonspherical long-range forces, and their resulting capture rate constants compare favorably to trajectory calculations.<sup>110</sup> For some ion–molecule reactions, for which the molecular degrees of freedom are weakly coupled to the reaction coordinate, classical trajectory calculations show that recrossing of the dividing surface may be important, especially at high temperature.<sup>111</sup> Definitive calculations for neutral zero-intrinsic-barrier reactions, such as radical–radical reactions, require considering medium-range effects, such as force constant changes in bends, as well as long-range forces. Preliminary indications for radical–radical reactions and low-barrier atom–molecule reactions are that, in three-atom systems, recrossing of the variational transition state is more important than for tight, high barriers.<sup>43,94,112</sup> Systems with loose transition states sometimes have a second tighter free energy bottleneck too.<sup>112–114</sup> The competition of two or more free energy bottlenecks can be handled by a unified statistical theory.<sup>38a,42,97,112,114–116</sup>

**Adiabaticity.** At 0 K, the generalized free energy of activation as a function of reaction coordinate, i.e., distance along the minimum-energy path, reduces to the vibrationally adiabatic ground-state potential curve, i.e., the sum of the Born–Oppenheimer potential along the reaction path and the zero-point energy. In the absence of a tun-

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neling correction, the threshold energy of variational transition-state theory is the maximum of the vibrationally adiabatic ground-state potential curve. The successes of variational transition-state theory, as summarized briefly above, imply that real systems tend to have an energy requirement at the dynamical bottleneck that can be well approximated by calculating a zero-point energy as if the generalized transition state were a real bound state. In many cases, though, variational transition-state theory yields good results even though the classical criteria for vibrational adiabaticity are violated, i.e., when the vibrational motion is not fast relative to the reaction-coordinate motion. Quantal adiabaticity, or near adiabaticity, is more easily achieved because of the finite energy-level spacings corresponding to bounded motions in quantum mechanics, and this is very important for the success of the theory. More detailed studies of vibrational and rotational adiabaticity as functions of the reaction coordinate in three-dimensional reactions would be valuable. Transition-state theory does not require that the system be vibrationally adiabatic all the way from reactants to the transition state, although that would be helpful in minimizing the tendency for snarled dynamics leading to recrossings of the transition state, but just that the rate constants be the same as calculated by quantizing the bound degrees of freedom at the assumed bottleneck.<sup>11,12,117,118</sup>

*Tunneling.* We mentioned in section 2 that as of 1973 there was no reliable method for including tunneling effects in transition-state theory. The first successful breakthrough was by Marcus and Coltrin,<sup>119</sup> who considered the collinear H + H<sub>2</sub> reaction. They used an approximate analytic continuation of classical mechanics to complex momenta because imaginary momenta, and hence negative kinetic energies, provide a classical analogue for tunneling. Then they sought a path that minimizes the imaginary part of the action integral, which corresponds to exponential decay of the wave function in tunneling regions. This was joined at the classical turning point of the reaction coordinate to a vibrationally adiabatic trajectory. The vibrationally adiabatic approximation was also used for the effective Hamiltonian along the tunneling path within the ground-state vibrational amplitude. The resultant optimal path was located at the curve of vibrational turning points on the concave side of the reaction path in the tunneling region. This corresponds physically to the negative internal centrifugal effect mentioned in section 2. The calculations were carried out using curvilinear coordinates referenced to the reaction path; these are called natural collision coordinates.<sup>35</sup> For large reaction-path curvature natural collision coordinates become multiple valued in physically accessible regions and the method breaks down. For large reaction-path curvature the physical approximation of vibrational adiabaticity also breaks down. This is often more serious for the tunneling correction than for the variational calculation with classical reaction-coordinate motion because the variational calculation is equivalent to making an adiabatic approximation only at the bottleneck, which tends not to be in a large-curvature region, but vibrationally adiabatic tunneling methods require vibrational adiabaticity over the whole reaction coordinate.

The Marcus-Coltrin-path adiabatic method was generalized to three-dimensional atom-diatom reactions with collinear reaction paths, and it was applied successfully

to several test cases.<sup>12,94,96,101,120</sup> Then a completely general version for any number of atoms in any number of dimensions that effectively avoids multiple-valued regions of natural collision coordinates and smooths out "bubbles" in the Marcus-Coltrin path was developed.<sup>106</sup> This is the small-curvature adiabatic approximation. The small-curvature adiabatic ground-state approximation corresponds to tunneling through the ground-state potential barrier of the adiabatic theory of reactions with an effective reduced mass that accounts for the shortening of the tunneling path by the negative internal centrifugal effect. The tests against accurate quantal calculations that were discussed above show that the small-curvature approximation gives a quantitatively reliable description of tunneling processes for many systems of interest with small and intermediate reaction-path curvature. A systematic analysis of tunneling approximations for such cases has been presented, along with a validity criterion for the small-curvature approximation or the use of natural-collision-coordinate-based tunneling methods.<sup>106</sup>

As mentioned above, the curvature of the reaction path depends on the mass combination as well as the potential energy surface, and the transfer of a light atom between two heavy moieties always corresponds to large reaction-path curvature. A good physical model for this case is that the light atom tunnels suddenly between stationary heavy groups (or atoms). Semiclassical approximations based on this idea have been suggested by Shushin and Ovchinnikova,<sup>121</sup> Babamov, Marcus, and Lopez,<sup>122</sup> and Garrett et al.<sup>107</sup> Garrett and co-workers call this the large-curvature approximation and have demonstrated its reliability by comparisons to accurate quantal calculations.<sup>105</sup> The numerical comparisons to accurate quantal calculations in the fourth paragraph of this section are based on the small-curvature-tunneling semiclassical adiabatic ground-state method for 30 of the 33 cases and on the large-curvature ground-state method for Cl + HCl and isotopic analogues. More recently Garrett and Truhlar<sup>123</sup> have developed a new method, called the least-action method, which is based on a least-imaginary-action principle. They numerically choose the best tunneling path for each energy from a parametrized sequence of paths between the reaction path and the large-curvature tunneling path. The tunneling path and the effective Hamiltonian along it are expressed in natural collision coordinates with the vibrationally adiabatic approximation near the reaction path, but in Cartesian coordinates without the adiabatic approximation when either natural collision coordinates or vibrational adiabaticity becomes invalid. With the new method they have obtained results more uniformly valid than the Marcus-Coltrin-path or small-curvature adiabatic approximations or the large-curvature approximation for a range of problems involving small, intermediate, and large reaction-path curvature. It appears that the practical problem of estimating tunneling contributions, given the potential energy surface, is largely solved, at least for accuracies of a factor of 2 or better at temperatures of 250 K or higher. It would, however, be desirable to place the empirically successful tunneling methods on a firmer theoretical footing.

Another approach to calculating the transmission

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coefficient is to base it on an exact quantal calculation for a problem with reduced dimensionality.<sup>31,32,124,125</sup> Bowman and co-workers<sup>124,125</sup> have recently applied this procedure to atom-diatom reactions with collinear minimum-energy paths.

**Anharmonicity.** Several studies have now shown the importance of anharmonicity, especially of low-frequency, large-amplitude motions, for the calculation of accurate rate constants.<sup>92,95,96,101,126</sup>

**Applications.** The applications of variational transition-state theory discussed above are primarily based on semiempirical potential energy surfaces. The large variational correction obtained with such surfaces for symmetric-barrier reactions with large reaction-path curvature has been confirmed by applying variational transition-state theory to  $^{37}\text{Cl} + \text{H}^{35}\text{Cl} \rightarrow \text{H}^{37}\text{Cl} + ^{35}\text{Cl}$  on an ab initio potential energy surface.<sup>107</sup> With classical reaction-coordinate motion in both cases, the conventional transition-state-theory rate constant exceeds the improved-canonical-variational-theory one by a factor of 28 at 300 K. Nonadiabatic tunneling plays an important role in this case, and as a consequence of the location of the variational transition state and the nature of the tunneling, the magnitude of the rate constant is controlled primarily by regions of the potential surface significantly displaced from the saddle point.<sup>105</sup> Another example of applications with ab initio surfaces is to  $\text{H} + \text{H}_2$  and isotopic analogues. This is the one system for which the ab initio potential energy surface is reasonably reliable<sup>127</sup> and the predictions of the theory are in good agreement with experiment for all isotopes for which rates are available.<sup>93,101,104,108</sup>

The applications of transition-state theory that we have discussed in detail so far are concerned with atom-diatom reactions, but one of the advantages of variational transition-state theory and the small-curvature and least-action tunneling models is that they are applicable to systems with many atoms. This is facilitated by using the reaction-path Hamiltonian of Miller et al.<sup>128</sup> They provide convenient equations for determining the harmonic vibrational frequencies and generalized normal modes within the surface orthogonal to the intrinsic reaction path. Isaacson and Truhlar<sup>95</sup> have used this Hamiltonian to formulate variational transition-state theory for polyatomics and have made an application to  $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ . Canonical variational theory differs significantly from conventional transition-state theory for this reaction and the effects can be understood by analogy to the reaction  $\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$ . As for atom-diatom reactions, tunneling was found to be very important, with a small-curvature adiabatic transmission coefficient of 17 at 300 K. This calculation employed a global fit<sup>129</sup> to an ab initio potential energy surface.<sup>130</sup> One advantage of variational transition-state theory with adiabatic transmission coef-

ficients is that one needs the potential energy surface only in the valley connecting reactants to products. By use of analytic gradient techniques<sup>131</sup> it is possible to efficiently calculate the potential energy surface only in this valley, without generating a grid of potential energy points spanning the full range of all coordinates.<sup>132,133</sup> Increasing use of this technique, especially in conjunction with generalized transition-state theory, can be expected. A difficult unsolved problem for polyatomic reaction rate calculations, however, is the development of a convenient and accurate way to include anharmonic coupling of vibrational modes.

Yamashita and Yomabe<sup>133</sup> have used ab initio gradient techniques to calculate vibrational frequencies as a function of reaction coordinate for the reaction  $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$ . The most rapidly varying frequency can again be understood by analogy to  $\text{Cl} + \text{H}_2$ . One may be able to generalize these trends and devise useful fitting functions for vibrational frequencies as a function of reaction coordinate. A simple attempt to do this has been reported recently.<sup>134</sup>

As mentioned in section 1, ab initio barrier heights are still too unreliable for most rate constant calculations, but progress in continuing on calculating transition-state-theory rate constants from ab initio input data for force constants with empirical values for the barrier heights. The recent calculations of Harding and co-workers<sup>135</sup> on  $\text{H}_2 + \text{C}_2\text{H} \rightarrow \text{H} + \text{C}_2\text{H}_2$  and  $\text{H} + \text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{HCO}$  illustrate the current status of this approach in a conventional transition-state-theory context. We look forward to the application of extended-basis-set large-CI techniques to calculate the reaction-path Hamiltonian for such systems over the whole important region of the reaction coordinate as required to calculate variational corrections and reliable transmission coefficients.

Kinetic isotope effects certainly constitute one of the most important fields of application of transition-state theory. Conversely, as stated in the first sentence of the excellent recent monograph by Melander and Saunders, "The theory of absolute reaction rates, or transition-state theory, forms the basis of almost all our discussions of isotope effects in chemical kinetics."<sup>136</sup> The simplifying feature of the calculation of equilibrium isotope effects is that, although the masses change, the force constants of the Born-Oppenheimer potential energy surface do not. Because a saddle point is a mass-independent feature of a reactive potential energy surface, conventional transition-state theory, by always placing the transition state at the saddle point, provides a way to extend this simplifying feature to kinetic isotope effects, and it yields a beautiful and elegant theory. However, variational transition-state theory often yields significantly different force constants for the optimized transition states of isotopically substituted systems.<sup>12,45,46,93,94,96,104,109,137</sup> Even the location of

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the maximum of the vibrationally adiabatic ground-state potential curve is usually isotope dependent. The isotope dependence of the variational transition states greatly complicates the theory of kinetic isotope effects. Another complication is provided by the nature of the successful tunneling calculations. For example the small-curvature approximation involves the vibrationally adiabatic ground-state potential curve, which is isotopically variant. The assumption that tunneling corrections can be computed from the isotope-independent Born-Oppenheimer potential along the minimum-energy path leads to large errors in many cases. An example of the way the new theories lead to a reinterpretation of kinetic isotope effects is provided by recent studies of the three-dimensional reaction  $^{37}\text{Cl} + \text{H}(\text{D})^{35}\text{Cl} \rightarrow \text{H}(\text{D})^{37}\text{Cl} + ^{35}\text{Cl}$ .<sup>107</sup> The conventional interpretation attributes the H/D kinetic isotope effect mainly to zero-point differences computed from saddle-point force constants. The new calculations attribute the kinetic isotope effect mainly to tunneling through regions of the potential energy surface far from the saddle point. Tests of the rate constants themselves against accurate quantal rate constants for the collinear reaction support the new interpretation.<sup>105</sup> Further work to sort out the isotopic dependence of transition-state structures and the effects of this dependence on the interpretation of kinetic isotope effects is very much needed.

Although transition-state theory is primarily directed to the prediction of thermal rate constants, the recent advances in generalized transition-state theory may also have more widespread influence. Some examples are the use of methods derived from generalized transition-state theory for the study of excited-state reactivity<sup>37,125,138</sup> and collisional resonances.<sup>103,139</sup> Another is the use of the reaction-path Hamiltonian for non-transition-state-theory scattering calculations.<sup>116,140</sup>

*Nonequilibrium Effects.* The discussion above is concerned with the calculation of equilibrium rate constants. Strictly these should be called local-equilibrium rate constants since they refer to a situation where all internal states of reactants are in equilibrium with each other, and the same for products, if present, but chemical equilibrium for reactants with products is not achieved.<sup>141</sup> The tests of conventional and variational transition-state-theory rate constants against quantal dynamics that have been reported are tests against accurate equilibrium rate constants for the same potential energy surface. Experimental rate constants though are obtained from phenomenological rate laws in a quasisteady state, i.e., following the decay of transients but not necessarily at local equilibrium. When phenomenological rate constants differ from equilibrium ones, we have the gas-phase analogue of the energy-transfer-limited regime discussed in section 2. Phenomenological rate constants are less than or equal to equilibrium rate constants. The deviation is expected to be small for slow reactions but reliable quantitative estimates for low-barrier reactions are not available. Most work on nonequilibrium effects for bimolecular reactions has been concerned only with translational disequilibrium. The most accurate results are apparently those of Present

and Morris.<sup>142</sup> They find, for example, an 8% effect for a case where the threshold energy is  $5kT$ , and smaller effects for higher threshold energies or lower temperatures. Lim and Truhlar<sup>143</sup> have estimated the internal-state nonequilibrium effect for the  $\text{Cl} + \text{HBr}$  reaction at 300 K by finding the quasisteady-state solution of the master equation with a set of realistic energy-transfer rates, including V-V energy transfer, and state-selected reaction rate constants. They obtain a nonequilibrium correction factor of 0.3. For this case the activation energy is about  $1.3kT$ .

*Rationale for Theoretical Comparisons.* Throughout this section we have emphasized comparisons of theoretical results for a given potential energy surface, and we have devoted very little space to comparisons to experiment. This is because the former kind of comparison may lead to direct information about the validity of various versions of transition-state theory, whereas in the latter we usually cannot unambiguously separate uncertainties in the potential energy surface from inadequate treatment of the dynamics. We think that the theoretical tests allow one to make realistic judgments about the expected validity of transition-state theory for various kinds of applications in interpreting experimental data, but, as stated in section 1, it is beyond the scope of this review to make a comprehensive survey of the applications.

#### 4. Gas-Phase Unimolecular Reactions

Unimolecular reactions involve many of the same effects as bimolecular reactions but also some new considerations.

*Choosing the Transition State.* Hase<sup>144,145</sup> and Troe and co-workers<sup>76,146</sup> recognized the significance of a variational criterion in interpreting experimental rate constants for unimolecular dissociation reactions without well-defined potential energy barriers and thereby resolved a controversy concerning the forward and reverse rate constants for the  $\text{C}_2\text{H}_6 \rightleftharpoons 2\text{CH}_3$  system.<sup>54,55,145</sup>

Some of the same considerations mentioned in section 3 for radical-radical and ion-molecule reactions<sup>44,110-112</sup> also apply to simple bond-scission reactions of neutrals and ion-molecule dissociations. As an example, the transition-state-theory expression for the rate constant for the radical-radical reaction  $\text{O} + \text{OH} \rightarrow \text{H} + \text{O}_2$  in the low-pressure limit is the same as the transition-state-theory expression for the rate constant for the reverse of the unimolecular reaction  $\text{HO}_2 \rightarrow \text{OH} + \text{O}$  in the high-pressure plateau region between low-pressure falloff and very-high-pressure diffusive behavior. However the accurate rate constants need not be the same for the two cases, and transition-state theory may be more valid for the high-pressure rate constant.

*Angular Momentum and Symmetries.* Conservation of angular momentum was not explicitly included in the initial development of RRKM theory. However, modifications have been introduced into the theory to account for angular momentum conservation to allow for more accurate testing of the fundamental assumptions against ex-

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periment.<sup>51-55,57,58,68,147-154</sup> Questions still remain about the effect of enforcing angular momentum conservation. For example, in most treatments of the dissociation of a symmetric top molecule only the conservation of the total angular momentum  $J$  is considered,<sup>76,155</sup> but classical trajectory calculations<sup>48,156-158</sup> indicate that for some reactions a projection  $K$  of the total angular momentum may also be conserved. In recent work Miller<sup>159</sup> has suggested that unimolecular dynamical effects may arise from geometrical symmetry conserved along the reaction path. This idea and the question concerning angular momentum conservation should receive considerable attention in future research.

**Computational Methods.** To allow for unimolecular decomposition at energies less than the vibrationally adiabatic barrier, the microcanonical unimolecular rate constant should be corrected for the effect of quantum-mechanical tunneling. Miller and co-workers<sup>155,160</sup> have reported tunneling calculations utilizing ab initio potential energy surfaces using a formulation<sup>12,97,155</sup> that has been called vibrationally adiabatic in the bimolecular context. Recent advances in calculating tunneling corrections for bimolecular reactions are also applicable here,<sup>97,106,123</sup> and one may expect to see them applied to unimolecular decompositions in the future. Moryl and Farrar have recently suggested that proton tunneling plays an important role in the reaction  $\text{CH}_3\text{OH}_2^+ \rightarrow \text{CH}_2\text{OH}^+ + \text{H}_2$ .<sup>161</sup>

**Anharmonicity.** In calculating the sum and density of states, one should take into account the complete anharmonicity of the potential energy surface. Hypothetically, anharmonic sums and densities can be found by first determining the energy levels for the anharmonic vibrational Hamiltonian (e.g., by diagonalizing the Hamiltonian with a sufficient basis set<sup>162-164</sup>) and then performing a direct count of states.<sup>165</sup> However, this method is impractical for Hamiltonians as complex as those of most real molecules.

There appear to be three different practical methods for introducing anharmonicity into the RRKM unimolecular rate constant. One method is to evaluate the classical anharmonic microcanonical rate constant either by a classical trajectory calculation<sup>58,68</sup> or by a Monte Carlo evaluation of the flux-coefficient form of transition-state theory with a "finite-width delta function".<sup>166,167</sup> The Monte Carlo transition-state method is particularly at-

tractive since trajectories do not have to be numerically integrated. It also is generalizable to a canonical ensemble.<sup>166</sup> However, the problem in calculating the anharmonic rate constant classically is that classical mechanics does not include the effects of quantal adiabaticity properly, and this may be a particularly severe problem at energies near the vibrationally adiabatic barrier.<sup>47,48</sup> The problem is enhanced as the number of degrees of freedom in the molecule is increased.

A convenient way for including anharmonicity is to represent the molecular Hamiltonian as a collection of separable anharmonic oscillators for which the quantum-mechanical energy levels are known.<sup>168,169</sup> Sums and densities of states are then found by direct count. The oscillators are usually assumed to be of the Morse type. This anharmonic correction is easy to make, but the accuracy of the separable anharmonic Hamiltonian is questionable.<sup>170</sup>

The third method<sup>58,171</sup> has not received wide use. However, it is of general applicability and initial work indicates it is quite accurate. In this technique the anharmonic sum of states for a potential energy function is determined classically by evaluating the multidimensional phase-space volume which is enclosed by the hypersurface  $H(q,p) = E$ .<sup>28,170-172</sup> The density is the first derivative of the sum of states. The quantal anharmonic sums and densities of state are then found by equating the classical ratios of anharmonic to harmonic values for the sum and density to the corresponding quantal ratios, an approximation first applied to partition functions by Pitzer and Gwinn.<sup>173</sup> The classical harmonic terms can be found analytically, while direct count is used to determine the quantal ones. This method also requires a separate estimate of the anharmonic effect on the zero-point energy. A recent application of this procedure illustrates the importance of anharmonicity which results from bend-stretch coupling.<sup>170</sup>

**Non-RRKM Behavior.** A breakdown in the RRKM theory can arise from a violation of either of its two postulates: (i) the existence of a dividing surface between reactants and products which trajectories do not recross; and (ii) the presence of a uniform density in the reactant's phase space. The latter assumption has received the most scrutiny. When the former has been investigated,<sup>48,68,156,157,174-177</sup> recrossing of a dividing surface has often been found to be unimportant for bond dissociation reactions; this, however, need not always be the case.<sup>111,112</sup> The importance of recrossing effects for isomerizations may depend on the complexity of the system.<sup>61,178</sup>

The second assumption of the RRKM theory requires that the reactant molecule have a random lifetime distribution.<sup>50,179</sup> The effect of violating this assumption was

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discussed by Rice.<sup>180</sup> He pointed out that, if there are restrictions in the reactant phase space so that all regions are not equally accessible, an initial microcanonical ensemble will *not* have a random distribution of lifetimes. Such an effect is referred to as *intrinsic* non-RRKM behavior.<sup>181</sup> The ensemble may be characterized by two or even more unimolecular rate constants. Slater<sup>59</sup> suggested that some trajectories may even be trapped in the reactant phase space and never dissociate. Such trajectories were labeled as "uninteresting"<sup>28,29,59,60</sup> in the mathematical sense, although of course they are really very interesting. If the trapped trajectories are confined to one region of the reactant phase space, the molecule still has a random lifetime distribution.<sup>61</sup> However, the unimolecular rate constant will be larger than that of RRKM theory by the factor  $1/f$ , where  $f$  is the fraction of the reactant phase space which consists of the chaotic type trajectories that will ultimately dissociate.

Failure of the random lifetime assumption also arises if the molecule is purposely excited nonrandomly, so that the initial decay rate will depend on where the excitation is deposited in the molecule. Such behavior is observed in chemical activation<sup>182-184</sup> and has been suggested in vibrational-overtone-excitation experiments.<sup>185</sup> Bunker and Hase<sup>181</sup> suggested that this effect be called *apparent* non-RRKM to distinguish it from intrinsic non-RRKM. If all parts of the reactant phase space are strongly coupled, the apparent non-RRKM behavior will only be present in the initial decomposition and the long-time decay will be characterized by the RRKM rate constant. The corrections to RRKM theory when the time scale for energy redistribution within the molecule is not much faster than the time scale for dissociation have been analyzed recently by Procaccia et al.<sup>186</sup> A novel recent example of nonstatistical laser chemistry is provided by the photodissociation of *n*-octylbenzene-argon van der Waals complexes, which dissociate at least 10 orders of magnitude faster than a Rice-Ramsperger-Kassel estimate.<sup>187</sup> This provides a striking demonstration of slow intramolecular vibrational randomization on the time scale of a dissociation.

From a fundamental quantum-mechanical point of view, unimolecular decay is really a problem in the decay of collisional resonances with overlapping widths.<sup>188</sup> Recent work has shown that model molecular Hamiltonians have trapped quasiperiodic trajectories above the unimolecular threshold, which can be quantized by primitive semiclassical methods.<sup>189,190</sup> By the relationship found between the classical and quantum mechanics of bound mole-

cules<sup>163,191-197</sup> the quasiperiodic trajectories are expected to represent compound-state resonances, and possibly have lifetimes significantly longer than that of RRKM theory. An important problem to be solved is to determine what types of potential energy surfaces give rise to long-lived compound-state resonances.<sup>198-201</sup> Another significant problem is the development of practical methods for determining the resonance width (i.e., lifetime).<sup>196,202-205</sup>

Whether a bound-state eigenfunction is spatially localized or not corresponds to some extent with whether or not the classical trajectories at the energy of the eigenstate are quasiperiodic or chaotic, but the correspondence between classical chaos, the nature of quantal eigenstates, and the regularity or irregularity of the quantal spectrum is not one to one.<sup>62,162,192-194,206</sup> A nonresonant quasiperiodic quantizing trajectory occupies only a limited region of the energetically accessible coordinate space, in accord with the probability density  $|\psi|^2$  for a localized quantum state. On the other hand, a chaotic trajectory covers all of the coordinate space as does  $|\psi|^2$  for a non-localized state, except that systems in symmetry-generated degenerate states will fail in the quantal case to transfer energy equivalently among equivalent phase-space locations.<sup>207</sup> Quasiperiodic trajectories above the unimolecular threshold, by necessity, can only have a limited extension along the reaction path. Thus, if there are levels just below the unimolecular threshold with localized wave functions that have small values of  $|\psi|^2$  along the reaction path, one would predict the presence of compound-state resonances. The question concerning the existence of compound-state resonances is then intimately related to the local or global nature of wave functions for highly vibrationally excited bound molecules. The calculations of Waite and Miller<sup>205</sup> indicated, perhaps surprisingly,<sup>208</sup> that, as the energy is raised, there is no connection between the transition from

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mode-specific to statistical behavior in quantum mechanics (even as  $\hbar \rightarrow 0$ ) and the transition from quasiperiodic to chaotic behavior in classical mechanics. More recent work<sup>209</sup> indicates that this may have been caused by the form of Waite and Miller's Hamiltonian, which does not favor mode-specific behavior, and that in other cases the two transitions are indeed related.

Though an amazing amount of progress has been made in our understanding of non-RRKM behavior, much work remains to be done. The relationship between the properties of wave functions for bound molecules and compound-state resonances presents a particularly exciting research area.

**Collisional Effects.** Experiments in the low-pressure limit and to some extent in the falloff regime show that for many reactions the strong collision assumption is incorrect.<sup>51-55,210</sup> For such situations a multistep activation and deactivation mechanism must be used, and this leads to a master-equation formalism for the unimolecular dynamics.<sup>51,52</sup> Considerable work has been done on approximate solutions to the master equation to account for weak-collider effects.<sup>169,211-216</sup> However, solutions which retain a quantitative description of the complete intermolecular and intramolecular dynamics are not available. Recent trajectory calculations indicate that such an effort may be necessary.<sup>217</sup> Another question which is expected to continue receiving considerable attention both theoretically and experimentally is the manner in which activation and deactivation transition probabilities are affected as the temperature (or energy) of the reactant is altered.<sup>218,219</sup> Given all the problems in formulating an accurate dynamical-theory procedure for calculating the thermal unimolecular rate constant, it has been proposed that simple semiempirical analytic functions be used to fit experimental  $k(T)$  vs.  $\omega_{\text{col}}$  curves.<sup>220</sup>

Recent work has shown that high-temperature systems reach the high-pressure plateau more slowly than expected from extrapolations at lower temperatures.<sup>221</sup> Lifshitz et al. have studied how the strong-collision assumption must be modified to account for this.<sup>222</sup>

**Applications.** The primary reason that the RRKM theory receives such wide use is that for most cases it has given a quantitative fit to unimolecular rate constants

measured thermally and by chemical activation.<sup>50-56</sup> In the RRKM calculations, vibrational frequencies and a structure for the transition state are chosen to match the entropy of activation determined from the Arrhenius frequency factor in the high-pressure plateau region. Two important thermal experiments where such agreement has been found are the isomerization reactions of cyclopropane<sup>223</sup> and methyl isocyanide.<sup>224</sup> Frequencies for the methyl isocyanide isomerization transition state have been determined by an ab initio calculation,<sup>225</sup> and they are in surprisingly good agreement with those hypothesized to match the entropy of activation. Unimolecular rate constants determined from chemical activation experiments for alkyl radicals,<sup>226</sup> alkyl halides,<sup>227</sup> and alkanes<sup>72</sup> are adequately interpreted by RRKM theory. For ethyl radical decomposition the use of an ab initio transition state in the RRKM calculation gives agreement between theoretical and experimental thermal rate constants.<sup>228</sup> The RRKM theory has been used widely in the interpretation of ion-molecule decomposition reactions.<sup>57,229</sup>

RRKM theory has also been used to interpret multiphoton infrared dissociation. In general, it is capable of explaining the data, but this does not appear to be a stringent test.<sup>230</sup>

Recently it has become possible to measure unimolecular rate constants of monoenergetically excited molecules and ions in the absence of collisions. Important work of this type has been performed by Troe, Crim, Zare, Baer, and co-workers.<sup>185,231-233</sup> An important finding is that the rate constants agree with RRKM predictions and are consistent with those from thermal and chemical activation experiments.

Though the above comparisons paint a rosy picture for the general applicability of RRKM theory, there still remain several concerns. Harmonic-state counting is almost always used in calculating the RRKM rate constant, and tunneling corrections are very seldom included. As more reliable ab initio potential energy surfaces become available so that more quantitative comparisons can be made with experiment, anharmonicity and tunneling should be included. One would hope that as the RRKM calculations become more precise, agreement between experiment and theory would be maintained. However, the opposite is certainly possible.

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There also remain several experimental studies which are not correctly interpreted with RRKM theory. Two examples for which the difference has been quantified are the mode selectivity observed in allyl isocyanide isomerization<sup>234</sup> and the paradox between the forward and reverse rate constants for the  $\text{H} + \text{C}_2\text{H}_2 \rightleftharpoons \text{C}_2\text{H}_3$  system.<sup>235</sup>

Finally, because of the collisional and energy averaging of thermal and chemical activation experiments they do not provide unequivocal tests of the random lifetime assumption of the RRKM theory.<sup>58,200,236</sup> Also, the microcanonical unimolecular rate constant is not very sensitive to the presence of trapped trajectories in the reactant phase space.<sup>61</sup> Classical trajectory calculations show that there are molecular Hamiltonians that have a significant fraction of trapped trajectories above the unimolecular threshold.<sup>189,190</sup> Extremely important problems to be solved are the determination of the properties of the quantal analogue of the trapped trajectories.

## 5. Reactions in Solution

*Frictional Effects.* The impact of transition-state theory with its elegant simplicity has perhaps been greatest for reactions in solution. In particular, the concepts of the transition state and the quasithermodynamic formulation of the rate, with its emphasis on free energy of activation, have been indispensable weapons in the arsenal of the practicing condensed-phase kineticist. Several fine textbook discussions attest to this.<sup>67,90,237-239</sup> None the less, while most reactions occur in solution, the investigation of the validity of transition-state theory in solution has noticeably lagged the corresponding question in the gas phase. But this has changed dramatically in recent years, and the concepts and applicability of transition-state theory for solution reactions have come under intense scrutiny.<sup>240</sup>

At first glance, transition-state theory would seem to be unassailable for solution rates—the fundamental equilibrium assumption appears to be on firm ground here, due to the frequent collisions of the reacting system with the solvent molecules. Yet this view both over- and underestimates the effect of solvent. For despite the high collision frequency in a dense solvent, vibrational energy equilibrium need not hold at the transition state. On the other side of the coin, frequent solvent collisions could severely interfere with the free unimpeded barrier passage assumed by transition-state theory. The quantification of these effects may be carried out in the framework painted by Kramers.<sup>79</sup> At low friction, the rate lies below the transition-state-theory prediction and increases with friction. At intermediate friction, transition-state theory may be a reasonable approximation, in which case the rate is independent of friction. As the friction increases still further, transition-state theory will again begin to overestimate the rate, which will decrease with friction, eventually reaching the diffusion-controlled regime where it is

inversely proportional to  $\zeta$ . The contrast of the energy-transfer-limited and friction-limited regimes with the transition-state-theory regime is clear: the rate constant will generally depend on the solvent dynamics, and it will vary nonmonotonically with friction, i.e., with some measure of the coupling to the solvent such as density, pressure, or viscosity. One important consequence of this, stressed by Troe<sup>241</sup> and Montgomery et al.,<sup>24</sup> concerns quasithermodynamic activation parameters such as the volume of activation. If the rate is yoked inappropriately into a transition-state-theory format, these parameters will actually contain a nonthermodynamic, solvent-dynamic contribution that can be quite significant. While Kramers theory provides a very rough outline of solvent effects, the sources and extent of the deviation from transition-state theory that it suggests can only be clarified by recent efforts, as discussed below, that are more attuned to a molecular view of the reacting system and the solvent.

*Static Solvent Effects.* Before we describe modern investigations of the influence of solvent dynamics on the validity of transition-state theory, we need to be concerned with static, or equilibrium, solvent effects. The static influence of the solvent on a rate constant can be understood via transition-state theory in its quasithermodynamic form.<sup>3</sup> Activation energies, activation entropies, and activation volumes depend on the solvent. This can be quite important since, as stressed in section 1, rates are very sensitive to barrier heights. Older estimates of such effects based on approximate free-volume models of liquids suggest that atom-transfer rates can be accelerated in solution by a factor between 10 and 50, while unimolecular isomerizations should not show much effect.<sup>242</sup> The large effect in the former case is due to the "pressure" of the dense solvent favoring the smaller particle separations in the transition state compared to the separated reactants. In the language of solution structure theory,<sup>243</sup> the solvent potential of mean force should replace the Born–Oppenheimer potential in the activation energy. Applications of these ideas to actual reactions<sup>244</sup> is complicated by the necessity to consider specific and competing effects of complexing, solvation, restriction of motion, and free-volume changes, as well as frequency of collisions as discussed below.

Chandler and Pratt<sup>245</sup> have developed methods for including potential-of-mean-force effects in reaction equilibrium constants in liquids. Ladanyi and Hynes<sup>246</sup> have extended this to atom-transfer transition states and calculate large solvent enhancements (up to a factor of 35) of transition-state-theory rate constants for solution reactions, particularly when the transition state is tight. Calculated solvent effects on isomerization transition states are much smaller,<sup>245-247</sup> usually small fractions of a kcal/mol. The same is true of unimolecular dissociations—static solvent structural cage effects arising from the mean potential are rather small: solvent cage barriers and wells for  $\text{I}_2$  lie in this range.<sup>248</sup>

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Very large static solvent effects on activation parameters are expected for charge-transfer reactions, due to strong interactions, up to hundreds of kcal/mol in strength, between charged species and polar solvents. The well-known Hughes-Ingold picture<sup>249</sup> of solvent polarity effects on reaction rates is based on equilibrium transition-state-theory solvation ideas. Large-scale simulations of solvent structure in aqueous media are now feasible,<sup>250</sup> and the modern equilibrium theory of polar solvents has seen considerable progress;<sup>251</sup> these techniques ought to be exploited to calculate transition-state-theory rate constants. So far, however, there have been very few calculations that go beyond the unreliable continuum dielectric approach. Two examples are the work of Warschel<sup>252</sup> on enzyme reactions and acid dissociation and the work of Calef and Wolynes<sup>253</sup> on the barrier heights for electron transfers in polar solvents. In both cases solvent effects are considerable and are poorly described by continuum dielectric pictures. Actually the notion of equilibrium solvation of a reaction transition state is a tricky one to which we return below.

*Dynamic Solvent Effects.* We now turn to the influence of solvent dynamics on the validity of transition-state theory. The most significant progress on understanding the role of solvent dynamics on the validity or breakdown of transition-state theory in solution has been achieved in studies based on time-correlation-function approaches for condensed-phase reactions. Chandler, Berne, and co-workers have developed and applied a formalism that is based on the reactive flux through a transition-state dividing surface.<sup>23-25</sup> Northrup and Hynes<sup>254</sup> have developed a different time-correlation-function approach, the stable-states picture, which can be applied to a wide variety of reactions using one or two surfaces as appropriate.<sup>78</sup> Somewhat different time-correlation-function formulas for reaction rates have been used by Skinner and Wolynes<sup>77</sup> and Stillinger.<sup>255</sup> There is thus a wide variety of approaches available for various problems, and different choices can be selected as more suitable for different applications and for investigations of the dynamical transmission coefficient. Most attention has been focused on models for the effect of bath particles, since full molecular dynamics simulations<sup>25-27,256-263</sup> of reactive systems sur-

rounded by many-body baths are still rare. Just as the rapid advances in quantal collision computations are playing an increasingly important role in our understanding of the validity and breakdown of transition-state theory in the gas phase, we expect full simulations to play an increasingly important role in solution. So far however the trends suggested by model treatments of the bath degrees of freedom seem to be supported by several of the full simulations. The model treatments of bath coordinates can be used in computer simulation of reactions (stochastic trajectory studies) to diminish or circumvent completely the need to simulate both the reaction system and all the surrounding molecules. Also they can be used to construct analytic theories which exhibit important trends. An important consequence is that we are at the stage of discovering phenomena associated with the breakdown of transition-state theory in solution, but not yet at a point where precise rates or solvent effects on rates can be predicted with any confidence.

Two basic types of models have been most widely used. One is an impulsive model, sometimes called the BGK model, in which velocity distributions are randomized to Maxwellians at every collision.<sup>24,25,77,264-267</sup> The other is a frictional model in the spirit of the Langevin equation, the Fokker-Planck equation, and the original approach of Kramers.<sup>78,268-277</sup> An important generalization of this is the generalized Langevin-equation description in which the solvent response is described by a molecular-time-scale time-dependent friction coefficient.<sup>78,278</sup> It has been shown<sup>78</sup> that a generalized Langevin equation leads to a dependence of reaction rates on the short-time solvent friction experienced by the reacting system, and not on the friction constant  $\zeta$ . This has important implications for the validity of transition-state theory, since the former is usually far less than the latter. Other stochastic models are also available.<sup>77,279</sup>

Much recent attention has been given to isomerization reactions in solution. Collisional kinetic models have been

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applied analytically<sup>77</sup> and in stochastic trajectory studies.<sup>24,25</sup> The trends are generally those of Kramers theory,<sup>79</sup> i.e., a nonmonotonic variation of the rate with solvent coupling, but with one important difference. In these models, energy activation and deactivation are less efficient than envisaged by Kramers. As a result, the transition-state-theory plateau is not reached with increasing friction before the rate starts to decrease due to solvent-induced recrossing. This shortfall is most extreme in cases where energy relaxation is slow and collisional momentum transfer is efficient. Thus, a calculation by Skinner and Wolynes<sup>77</sup> for a light reacting system in a solvent of massive particles (Lorentz limit), where these conditions apply, yields a very small maximum dynamical transition coefficient of order 0.1. In contrast a BGK impulsive model gives a maximum dynamical transmission coefficient of 0.6, and a Kramers Langevin-equation model gives 0.9–1.<sup>77,280</sup> The Langevin-equation approach becomes more valid for heavy solutes in light solvents. A more specific example is the butane isomerization which has been studied extensively by Chandler, Berne, and co-workers.<sup>24,25</sup> They find by full molecular dynamics simulation a dynamic transmission coefficient of about 0.4 at liquid-state densities. This is in reasonable agreement with a Kramers estimate for this system. However the short-time dynamics predicted by a stochastic simulation corresponding to Kramers theory does not agree well with the full molecular dynamics simulation. The full molecular dynamics simulation corresponds most closely to the low-friction limit of a BGK stochastic treatment.<sup>24,25</sup>

How often the rate as a function of friction actually plateaus noticeably below transition-state theory in real isomerizations is as yet unclear. But it is clear that the solution-phase analogue of the unimolecular falloff regime where the rate increases with solvent coupling definitely occurs in solution isomerization. Hasha, Eguchi, and Jonas<sup>281</sup> find experimentally that the conformational inversion of cyclohexane is accelerated with increasing solvent pressure to an extent greater than that estimated from thermodynamic activation effects, a result in accord with the prior theoretical results for the low-friction BGK regime.<sup>24,25,77</sup> The dependence of the rate constant on collision frequency seems to be well described by a BGK model for a potential with narrow wells and a wide barrier.<sup>282</sup> For another example, Troe and co-workers<sup>241,283</sup> have found that the rate of iodine recombination in compressed rare gases remains third order up to very high pressures, greater than 100 atm. The switchover from the third-order energy-transfer-limited regime to the second-order diffusion-influenced regime occurs at densities of the order of liquid densities. These examples show that the low-friction, activation-controlled regime may sometimes apply even at liquid-phase collision frequencies so that the transition-state theory overestimates the rate constant because of the equilibrium assumption.

It has been emphasized<sup>284,285</sup> that such energy-transfer-limited behavior can be traced to inefficient vibrational energy transfer between the reacting system and the solvent. What counts for the energy transfer is the spectrum

of solvent forces at the usually high vibrational frequencies of the isomerizing molecule.<sup>284–288</sup> At such frequencies, the solvent forces are much less effective in inducing vibrational energy transfer than would be estimated from simple collisional or frictional models. This suggests that energy-transfer-limited isomerizations might occur often in solution, particularly in fast, low-barrier reactions. It also appears likely that solvent properties such as internal molecular structure will often be more important than, e.g., viscosity.

There has also been a large body of work on isomerizations in the regime where the rate constant decreases with friction. Experimental studies of dibenzyl ether,<sup>289</sup> diphenylbutadiene,<sup>290</sup> the organic dye DODCI,<sup>290</sup> and stilbene<sup>291</sup> show that transition-state theory breaks down by the rate decreasing with measures of solvent coupling such as viscosity. But it is found by Goldenberg et al.<sup>289</sup> that Kramers theory does not explain the viscosity dependence of the apparent activation energy and by Fleming and Hochstrasser and co-workers<sup>290,291</sup> that the rate does not vary simply as the inverse friction of viscosity at high viscosity, as in Kramers theory. Bagchi and Oxtoby<sup>292</sup> have applied the Grote-Hynes generalized Langevin-equation approach<sup>78</sup> to the DODCI experiments<sup>290</sup> and shown that the short-time friction coefficient concept explains this behavior. Clearly the short-time nonhydrodynamic behavior of the solvent is important.

A key distinction between isomerizations and atom-transfer reactions is that there are no or very small reactant and product wells on either side of the barrier in a typical atom-transfer case. Because of this, weak coupling to solvent will often be less important for bimolecular than for unimolecular reactions. With respect to strong-coupling solvent effects on atom-transfer reactions, it has been emphasized by Grote and Hynes<sup>293</sup> that, for the case of sharp barriers, the relevant short-time solvent friction is rather small, and transition-state theory will often be a good approximation. It has been shown<sup>294</sup> in a model calculation for sharp-barrier atom transfers that the rate is essentially impervious to increasing the long-time-scale hydrodynamic friction. This may explain the experimental results of Rossman and Noyes,<sup>295</sup> who found that the rate of radioactive iodine exchange with vinyl iodide changed little from *n*-hexane solvent to hexachlorobutadiene solvent—a 100-fold increase in solvent viscosity. Again, the short-time-scale behavior is crucial in assessing the validity of transition-state theory.

Weak-bath-coupling effects may be important for some bimolecular reactions in solution. For example, Allen<sup>296</sup> has found in a stochastic simulation of a low-barrier atom-transfer reaction that the rate constant increases with friction. Internal-state depletion effects such as may be observed in gas-phase diatomic dissociation<sup>297,298</sup> and atom-transfer reactions<sup>143,299</sup> may also sometimes be im-

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portant in solution.

Charge-transfer reactions, such as  $S_N2$  displacements, proton transfer, and ion-pair interconversions, present an important question for transition-state theory, which assumes in the standard approach that the transition state has an equilibrium solvation, as discussed above, and that the solvent plays no role in the reaction coordinate. But it is certainly not clear that the required reorientational relaxation of solvent dipoles is always sufficiently fast for equilibrium solvation to apply. Stated another way, if solvent reorientation—dielectric relaxation—plays a role in the reaction, then we should think in terms of “nonequilibrium” solvation.<sup>300</sup> The rate will depend on solvent reorientation rates, and the standard transition-state-theory description will break down. This question has been investigated by van der Zwan and Hynes<sup>301</sup> in a model study of a charge-transfer reaction. The dynamic polar solvent influence is accounted for by a generalized Langevin-equation description. For broad-barrier reactions and strongly polar and slowly relaxing solvents, solvent reorientation becomes rate limiting; i.e., nonequilibrium solvation is extreme: transition-state theory fails badly, and the rate is inversely proportional to the solvent reorientation time. In this limit, rates may show important  $H_2O/D_2O$  solvent isotope effects, reflecting isotope effects on solvent dielectric relaxation times.<sup>301,302</sup> In the opposite regime of sharp barriers and weakly polar solvents, the rate is fairly well described by transition-state theory; the chemical forces driving the reaction are strong enough to dominate the resisting solvent dipoles. Even when the solvent is slowly relaxing, the rate does not track the solvent dielectric relaxation time. It has also been shown that the solvent can be taken into account by including an additional coordinate besides the coordinate associated directly with the reacting system.<sup>303</sup> This leads to a reaction coordinate that depends on both the reacting system and the solvent. Including one or more degrees of freedom of the solvent as a part of the reacting system is a new approach to including dynamic solvent effects in generalized transition-state theory. It may be that some of the ideas of variational transition-state theory of section 3 can be used here to find the best dividing surface for calculating a transition-state-theory rate.

Related ideas arise in the theory of electron-transfer reactions in solution. The Marcus theory<sup>304</sup> of electron transfer in the adiabatic limit is a transition-state-theory result, and the dynamics of solvent reorientation play no role. Several workers<sup>305–307</sup> have recently stressed that

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transition-state theory may break down if there is slow solvent relaxation.

Although the emphasis so far on transition-state dividing-surface recrossings in solution-phase work has been on those due to solvent-induced motion, the same kinds of intrinsic dynamic effects that cause transition-state dividing-surface recrossings in gas-phase reactions must also be significant in many cases. Simultaneous inclusion of both kinds of effects could be achieved by applying stochastic trajectory methods to sufficiently complicated systems. This would be important to determine whether a breakdown of transition-state theory in any given case is due to intrinsic dynamic effects or to the solvent.

Interesting examples of how intrinsic and diffusional effects on the detailed dynamics may have mutual effects are provided in two recent studies.<sup>308,309</sup> For example, Northrup and McCammon<sup>308</sup> found that diffusive effects may lead to corner cutting similar to the negative internal centrifugal effect that may occur because of intrinsic dynamics in the gas phase.

The influence of the solvent on quantum tunneling has also been studied at the model level. The key result of the recent work of Sethna,<sup>310</sup> Wolynes,<sup>311</sup> and Harris and Stodolsky<sup>312</sup> is that dynamic solvent interaction reduces tunneling. In contrast, Korst and Nikitin<sup>298,313</sup> find that the effect of friction may be in either direction, and Cribb et al.<sup>314</sup> find under certain circumstances an enhanced rate of tunneling for a model including stochastic interaction with the environment. In still other work there is a controversy about the role of solvent reorganization in proton-transfer reactions.<sup>315–317</sup> One possible mechanism by which solvent interactions may increase the probability for tunneling is by converting a nonresonant situation into a resonant one. Delineation of the dominant effects of solvent on tunneling probabilities in various circumstances will certainly prove important for the interpretation of kinetic isotope effects in solution reactions. The effect of quantitation of the bound degrees of freedom on the considerations of this section also requires study.

Many of the concepts and methods discussed in this section can also be applied to transport processes, solid-phase reactions, and processes at surfaces, but these studies are beyond the scope of the present article.<sup>318–323</sup>

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## 6. Concluding Remarks

It is clear that our understanding of transition-state theory, when it is valid, and when it is not, has been advanced significantly in the last 5 years. It is encouraging that this research strengthens our sense that transition-state theory provides a useful conceptual framework for discussing chemical reactions under almost all conditions. Further research on corrections for nonequilibrium effects and on incorporation of more detailed dynamics, as well as on further delineating the range of validity of the uncorrected original theory, is anticipated optimistically. This work should make transition-state theory more useful for absolute rate calculations and also for interpretative purposes such as inferring mechanisms from kinetic isotope effects, correlating activation parameters with structural information, understanding pressure effects and solvent effects, and so forth. Furthermore, as generalized transition-state theories incorporate more and more of the

detailed dynamics, the distinction between statistical theories and collision theories begins to blur. Thus, it seems that, whatever the modern rate theories of the future may look like, they will probably always retain something of the elements of transition-state theory.

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