

# VARIATIONAL TRANSITION STATE THEORY METHODS FOR CALCULATING REACTION RATE CONSTANTS IN GAS AND CONDENSED PHASES

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## 1. Introduction

Transition state theory (TST) in its thermodynamic formulation<sup>1</sup> is the most widely used tool for analyzing rate constants of chemical reactions (for example, see Benson<sup>2</sup>). The dynamical formulation of TST<sup>3</sup> provides the best approach to examine the approximations in TST and the basis for systematically improving the conventional theory. Over the past two decades, significant progress has been made in developing methods for quantitative predictions of reaction rate constants based upon the dynamical formulation of TST (see reviews by Truhlar, Hase, and Hynes<sup>4</sup> and Truhlar, Garrett, and Klippenstein<sup>5</sup>). As an example, quantized variational transition state theory (VTST) with multidimensional, semiclassical tunneling corrections<sup>6-8</sup> are capable of accurate predictions of gas-phase rate constants.<sup>9,10</sup> The accuracy of the potential energy surface is typically the major factor limiting the accuracy of the calculated rate constants. In this paper we briefly review VTST methods and their application to gas-phase reaction. We also briefly outline an approach to extend these methods to treat reactions in solution.

## 2. VTST for Gas-Phase Reactions

In the dynamical formulation of TST, the classical equilibrium rate constant is derived using a single approximation, the fundamental assumption of TST.<sup>3,11</sup> A dividing surface is defined so that all reactive trajectories must pass through it. The fundamental dynamical assumption is then defined as follows: a reactive trajectory originating in reactants must cross the dividing surface only once and proceed to products. The TST expression for the rate constant can then be expressed using equilibrium statistical mechanics without the need to calculate classical trajectories. Classical trajectories that recross the dividing surface cause a breakdown of the fundamental assumption. All reactive classical trajectories must cross the dividing surface and these are correctly counted in TST. However, some nonreactive trajectories may also be counted as reactive so that TST provides an upper bound to the exact reactive flux of classical trajectories through the dividing surface. This is the basis of classical variational TST in which the definition of the dividing surface is optimized to minimize the rate constant.<sup>12-14</sup>

In VTST the dividing surface is viewed as a tentative dynamical bottleneck to flux in the product direction, and the best bottleneck (the dividing surface allowing the least flow of flux) is located variationally. A practical approach is to define the dividing surfaces to be orthogonal to the reaction path, where the reaction path is defined as the minimum energy path connecting the saddle point with both the reactant and product regions. The minimum energy path is located by following the path of steepest descents in both directions from the saddle point in a mass-weighted coordinate system such that each degree of freedom has the same effective mass in the kinetic energy expression. The generalized expression for the thermal rate constant for temperature  $T$  is given as a function of the location  $s$  of the dynamical bottleneck along the reaction coordinate

$$k^{GT}(T, s) = \sigma \frac{k_B T}{h} \frac{Q^{GT}(T, s)}{\Phi^R(T)} \exp(-V_{MEP}(s)/k_B T) \quad (1)$$

where  $\sigma$  is a symmetry factor,  $k_B$  is Boltzmann's constant,  $h$  is Planck's constant,  $Q^{GT}(T, s)$  is the generalized partition function for the bound degrees of freedom orthogonal to the reaction path at  $s$ ,  $\Phi^R(T)$  is the reactant partition function, and  $V_{MEP}(s)$  is the value of the potential along the reaction path at  $s$ . In conventional TST, the dividing surface is placed at the saddle point, defined by  $s=0$

$$k^{TST}(T) = k^{GT}(T, s=0) \quad (2)$$

Conventional transition state theory requires information about the potential energy surface only in the saddle point and reactant regions. In particular, the value of the potential at the saddle point (relative to the reactant value) is required, and if the partition functions are computed using a harmonic approximation, then the matrix of second derivatives of the potential energy with respect to mass-weighted coordinates (Hessian matrix) suffices. In one version of variational transition state theory, the canonical variational theory (CVT),<sup>15,16</sup> the rate constant expression in eq. (1) is minimized with respect to  $s$

$$k^{CVT}(T) = \min_s k^{GT}(T, s) \quad (3)$$

The improved canonical variational theory (ICVT)<sup>17</sup> also variationally optimizes the location of the transition state dividing surface for a given temperature, but provides an improved treatment of threshold energies by using an ensemble which removes energies below the ground-state adiabatic threshold. To compute the rate constant using either the canonical or improved canonical variational theory, more information about the potential energy surface is required than for a conventional transition state theory calculation; information about the potential in a region around the reaction path is also required. For a harmonic treatment of the partition functions, the Hessian matrix along the minimum energy path will suffice. In this case the potential information needed is the energy and its first and second derivatives along the minimum energy path.

For many reactions of practical interest, particularly those involving hydrogen atom transfer, quantitative accuracy in computed rate constants requires that quantum mechanical effects be included in the theory. However, the fundamental assumption is inherently a classical approximation since it requires knowledge of both the coordinate and momentum (or flux) at the dividing surface. Additional approximations are needed to include quantum mechanical effects into TST. The standard approach is a separable approximation<sup>1,18</sup> that replaces classical partition functions by quantum mechanical ones and includes a correction factor for quantum mechanical motion along the reaction coordinate (e.g., tunneling). The failure of this approach has been attributed largely to nonseparable effects, particular on quantum mechanical tunneling.<sup>19,20</sup> The development of multidimensional tunneling correction factors that are consistent with variational transition state theory was greatly facilitated by the realization that the adiabatic theory of reactions is equivalent to one form of variational TST (microcanonical VTST).<sup>15,16</sup> In this approach, the partition functions in eq. (1) are evaluated quantum mechanically, and quantum mechanical effects on the reaction coordinate motion (e.g., quantum mechanical tunneling) are included by a multiplicative factor – the transmission coefficient.

In VTST, it is consistent to treat tunneling as occurring through the vibrationally-rotationally adiabatic potential

$$V_a(s, \alpha) = V_{\text{MEP}}(s) + \epsilon_{\alpha}^{\text{GT}}(s) \quad (4)$$

where  $\alpha$  is a collective index of the quantum numbers for the bound modes and  $\epsilon_{\alpha}^{\text{GT}}(s)$  is the bound energy level for state  $\alpha$  at the generalized transition state located at  $s$  along the reaction path. For thermal rate constants the tunneling is approximated using only the ground-state adiabatic potential curve ( $\alpha=0$ ). The adiabatic approximation is made in a curvilinear coordinate system, and although the potential term is simple, the kinetic energy term is complicated by factors dependent upon the curvature of the reaction path. For systems in which the curvature of the reaction path is not too severe, the small-curvature semiclassical adiabatic ground state method<sup>21,22</sup> includes the effect of the reaction-path curvature to induce the tunneling path to 'cut the corner' and shorten the tunneling length. The small-curvature tunneling (SCT) probabilities  $P^{\text{SCT}}(E)$  are computed for energies below the maximum in the ground-state adiabatic potential curve (denoted  $V^{\text{AG}}$ ) where transmission occurs by tunneling and above  $V^{\text{AG}}$  where nonclassical reflection can diminish the transmission probability. The SCT transmission coefficient is given by the normalized Boltzmann average of  $P^{\text{SCT}}(E)$

$$\kappa^{\text{SCT}}(T) = \beta \exp(\beta V^{\text{AG}}) \int_0^{\infty} dE P^{\text{SCT}}(E) \exp(-\beta E) \quad (5)$$

where  $\beta=1/k_B T$ . Combining the SCT transmission coefficient with the improved canonical variational theory rate constant yields

$$k^{\text{ICVT/SCT}}(T) = \kappa^{\text{SCT}}(T) k^{\text{ICVT}}(T) \quad (6)$$

To construct the adiabatic potential, the type of potential information required is identical to that needed for the variational transition state theory calculation. For the SCT calculation it is also necessary to know the curvature of the reaction path which can be obtained from second derivatives of the potential along the reaction path. Thus, to provide a consistent and accurate estimate of the tunneling, no new information about the potential energy surface is required.

Accurate quantum rate constants for nearly forty gas-phase bimolecular reactions provide benchmarks to test the accuracy of the VTST calculations. VTST calculations, which include multidimensional tunneling corrections, have been tested against accurate quantal results for about 30 atom-diatom reactions in a collinear world and nearly 10 reactions in three dimensions. Conventional TST was found to be accurate within a factor of 2 for only about 25% of these systems and had errors larger than of 5 in about 25% of the systems. The VTST calculations were generally within 50% of the accurate results with errors less than a factor of two in all cases.

### 3. VTST for Solution-Phase Reactions

The computational procedures described above to perform VTST calculations require identification of a saddle point and a reaction path connecting the saddle point with reactants and

products. For reactions in solution, there can be many saddle points that are close in energy and that differ significantly only in the configuration of the solvent. The multiple saddle points are a reflection of the large anharmonicity in the solvent that makes the quantum mechanical calculation of the partition functions impractical. Procedures are outlined elsewhere<sup>23</sup> that allow VTST calculations, which are based upon potential energy surfaces and include quantum effects, to be extended to solution-phase reactions. In this approach the system is separated into a cluster model that contains the part of the system undergoing reaction and the solvent that is treated in an approximate manner. The coordinates of the cluster model are treated explicitly, and the effects of the extended solvent are approximately included in an effective Hamiltonian. The constant proximity of solvent molecules around the solute changes the interaction potential within the solute. The resulting mean field potential for the solute is obtained from an equilibrium ensemble average over solvent configurations. Since this mean field potential is obtained from an equilibrium ensemble average at each solute configuration, the equilibrium solvation assumption implies that the solvent molecules instantaneously equilibrate to each new solute configuration. Effects of solvent fluctuation from their equilibrium values upon reaction dynamics are included using a reduced-dimensionality model that introduces a limited number of additional degrees of freedom in the effective Hamiltonian.

This approach for including solvation effects requires explicit treatment of only a limited number of degrees of freedom and information about the effective potential energy surface for these explicit coordinates is needed only in the region of a reaction valley. Explicitly treating only a limited number of coordinates obviates some of the difficulties inherent in quantum mechanical TST calculations on solution-phase reactions (e.g., the multiple saddle point problem) and also allows the quantum mechanical effects to be included by the standard gas-phase procedures outlined above. These procedures are computationally intensive, but given the recent advances in computational hardware and software, these calculations are possible.

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