CHEMICAL DYNAMICS AT LOW TEMPERATURES

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VOLUME LXXXVIII

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INTRODUCTION

Few of us can any longer keep up with the flood of scientific literature, even in specialized subfields. Any attempt to do more and be broadly educated with respect to a large domain of science has the appearance of tilting at windmills. Yet the synthesis of ideas drawn from different subjects into new, powerful, general concepts is as valuable as ever, and the desire to remain educated persists in all scientists. This series, *Advances in Chemical Physics*, is devoted to helping the reader obtain general information about a wide variety of topics in chemical physics, a field which we interpret very broadly. Our intent is to have experts present comprehensive analyses of subjects of interest and to encourage the expression of individual points of view. We hope that this approach to the presentation of an overview of a subject will both stimulate new research and serve as a personalized learning text for beginners in a field.

ILYA PRIGOGINE
STUART A. RICE

PREFACE

Chemical dynamics at low temperatures is connected with elementary reactions that surmount potential energy barriers separating reactants from products in the absence of thermal activation. The first experimental evidence of this type of reactions was obtained in the early 1970s in studies of solid-state conversion of free radicals. These investigations clearly demonstrated that there is a sufficiently sharp transition from Arrhenius-like exponential temperature dependence, characteristic of thermal activation, to much weaker power-like temperature dependence down to the low-temperature limit of the rate constant.

In principle, the explanation of this phenomenon was known to be associated with tunneling through a barrier. Only after a substantial body of experimental data was accumulated were adequate models developed that elucidated the multidimensional character of tunneling and the effects of nontunneling intra- and intermolecular vibrational modes. Similar ideas have been considered independently in the quantum transition-state theory, which has been applied mainly to gas-phase reactions proceeding in the region below the energetic threshold. The supersonic jet cooling technique, in combination with high-resolution molecular spectroscopy, has revealed numerous examples of multidimensional tunneling in isolated molecules and dimers.

There are a number of specialized reviews covering the advances in each of these separate areas of research, but there is now a need for a survey of the entire field. The joint consideration of multidimensional tunneling and its manifestation in the various branches of chemical physics can provide theoreticians with a guide to a huge set of yet unsolved problems to which modern quantum mechanical methods can be applied. Experimentalists need information about the deep analogies between tunneling phenomena taking place in a variety of fields that, at first sight, might seem unrelated. Our goal is to address both of these needs, which dictates the structure of the current volume and the choice of materials.

In the first chapter, the history of the development of chemical dynamics at low temperatures is surveyed. The formulation of general problems and the main approximations used to solve them are given. The second chapter considers specific features of tunneling chemical dynamics. The results are presented without derivation. The third chapter

contains a consistent description of one-dimensional tunneling in the path integral formalism. The more traditional consideration of the same problem in the WKB approximation is given in Appendix A. This chapter is designed for newcomers to the study of the quantum theory of chemical reactions. The fourth and fifth chapters are devoted to special problems of two- and multidimensional tunneling. Readers who are not interested in theoretical aspects can skip these two Chapters, because Chapter 2 contains the basic information necessary for understanding Chapters 6–9, in which pertinent experimental results are presented.

We are grateful to V. I. Goldanskii, who was the initiator of the investigation in this field, W. H. Miller., N. Makri, and D. Truhlar for useful advice, which helped us in selection of materials, and our collaborators, P. Grinevich, E. Ya. Misochko, and T. J. Tague, Jr., for support and discussions. One of us (V.A.B.) is grateful to the National Science Foundation for support and to the University of Utah for hospitality while this volume was being written. Finally, we are indebted to Anna Tapia and Alexander Benderskii for their skillful assistance in the preparation of the manuscript.

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January 1994

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INTRODUCTION

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1.1. HISTORICAL BACKGROUND

Every chemical reaction involves the rearrangement of chemical bonds. Under ordinary circumstances, the reactants and products are stable on the time scale of their vibrational frequencies. In this respect they represent quasistationary states, and the reaction itself is associated with surmounting an energy barrier that divides them. The stability of the reactants under thermal conditions implies that the population distribution among their energy levels is close to equilibrium. For this to take place, the barrier height should be greater than both the thermal energy and the energy level spacing; that is

$$V_0 \gg \hbar\omega_0 \qquad \beta V_0 \gg 1 \qquad \beta = (k_B T)^{-1} \tag{1.1}$$

Under these conditions the rate constant is determined by the statistically averaged reactive flux from the initial to the final state.

The quintessential expression of classical chemical kinetics is the Arrhenius law:

$$k(T) = k_0 \exp(-\beta V_0) \tag{1.2}$$

The rate constant in this expression can be interpreted loosely as some characteristic attempt frequency multiplied by a Boltzmann factor, which represents the probability of occupying the initial states that lie just above the top of the barrier. The Arrhenius law predicts that even for the lowest barrier still satisfying Eq. (1.1) the rate constant vanishes at sufficiently low temperature. For instance, even for a very fast reaction with $k_0 = 10^{13}\,s^{-1}$, $V_0 = 1.2$ kcal/mol, $k = 10^{12}\,s^{-1}$ at 300 K, the rate constant decreases to $\leq 10^{-9}\,s^{-1}$ at $T = 10$ K. Such a low value of k completely precludes the possibly of measuring any conversion on a laboratory time scale.

Quantum mechanics brought new essential features to chemical reaction theory. First, the nature of the chemical bond itself has been established, and the concept of a potential energy surface (PES) on which the chemical reaction occurs has been introduced. Second, the partition functions for quantized states of the reactants and products were considered in the development of classical transition state theory (CLTST) [Eyring, 1953; Eyring et al., 1983; Glasstone et al., 1941]. This theory, developed originally by Eyring, treats only transitions that surmount the barrier with $E > V_0$. The history of CLTST has been written up by Laidler [1969]. A significant refinement of the theory was to postulate the existence of a transition state, or dividing surface, that defines a "point of no return" such that once a classical trajectory of free motion along the reaction coordinate crosses the transition state, it never returns to the reactant region [Miller, 1976; Wigner, 1938]. Third, quantum mechanics allows for tunneling, i.e., the penetration of particles through classically forbidden regions. This possibility was originally considered within CLTST only as giving rise to small corrections in the rate constant. Wigner [1932, 1938] was the first to calculate this correction for a parabolic barrier. He discovered that the apparent activation energy

$$E_a = k_B T^2 \frac{\partial \ln K}{\partial T} \tag{1.3}$$

becomes less than the barrier height and decreases with decreasing temperature, viz.,

$$E_a = V_0 - \frac{\beta}{24} (\hbar \omega_\#)^2 \tag{1.4}$$

where $\omega_\#$ is the characteristic frequency of the upside-down parabolic barrier

$$V(Q) = V_0 - \tfrac{1}{2} m \omega_\#^2 Q^2 \tag{1.5}$$

and the reaction coordinate Q is separated from the total set of degrees of freedom. It was noted earlier [Hund, 1927; Roginsky and Rozenkevitsch, 1930] that the tunneling corrections should be noticeable in the case of high and narrow barriers, and they should be taken into account for light particle transfer reactions (e.g., for hydrogen atoms). Bell's solution [Bell, 1933, 1935, 1937] to Wigner's problem for low temperatures ($\beta \hbar \omega_\# / 2\pi > 1$) demonstrated that at $T \to 0$ the rate coefficient is no longer subject to the Arrhenius law. However, this result was virtually unnoticed, partly because of the exotic nature of the experimental

conditions (for that time), and partly because of the apparently inappropriate form of the parabolic barrier (1.5) at $E \ll V_0$, where the potential should approach a minimum.

The next three decades were a period of overwhelming domination of CLTST, which became a universal basis for microscopic descriptions of gas- and liquid-phase chemical reactions. Tunneling was drawing little attention in the context of chemical kinetics during those years. Only Bell's long-term studies, summarized in his well-known books [Bell, 1973, 1980], ascertained the two main consequences of proton tunneling in liquid-phase reactions: the lowering of the apparent activation energy and growth of the H/D kinetic isotope effect with decreasing temperature. The same rules were found by the early 1960s in gas phase reactions of H atoms [Johnston, 1960]. In both cases tunneling was considered to occur from thermally activated reactant states just below the barrier top and to give rise only to small corrections to the Arrhenius law.

In 1959 Goldanskii showed that at sufficiently low temperatures (i.e., when the population of thermally activated energy levels vanishes), the sole contribution to the reactive flux consists of tunneling from the ground state, and the rate constant approaches its low-temperature quantum limit k_c, becoming temperature-independent [Goldanskii, 1959, 1979]. The transition from the Arrhenius region to the low-temperature plateau occurs over a relatively narrow temperature range determined by a characteristic temperature T_c, which has later been called the cross over temperature. It depends not only on V_0, but also on the barrier width d and tunneling mass m, viz.,

$$\beta_c^{-1} = k_B T_c = a\left(\frac{\hbar^2 V_0}{2md^2}\right)^{1/2} \tag{1.6}$$

In this expression d is the barrier width corresponding to the zero-point energy in the initial state, and the factor a is of the order unity depending on the barrier shape. It equals $1/2$, $2/\pi$, and $3/4$ for rectangular, parabolic, and triangular barriers, respectively, and is unity for a barrier constructed from two shifted parabolas. For the parabolic barrier (1.5), Eq. (1.6) assumes the form

$$k_B T_c = \frac{\hbar\omega_{\#}}{2\pi} \tag{1.7}$$

The low-temperature limiting rate constant k_c is related to V_0 and T_c through the approximate formula

$$k_c = Ak_0 \exp(-\beta_c V_0) \tag{1.8}$$

where the factor $A \sim (\beta_c V_0)^{-1}$ accounts for the decrease in $k(T)$ in the intermediate region between the Arrhenius dependence and low-temperature plateau. As follows from (1.6)–(1.8), the rate constant of the tunneling reaction, unlike the classical case, depends not only on the barrier height, but on the additional parameter $\hbar^2/2md^2$ (or $\hbar\omega_\#$), which does not appear in CLTST. The dependence of k_c on this parameter is as strong as on V_0. For example, k_c can vary by more than 10–12 orders of magnitude using typical ranges of d and m ($d = 0.5$–2.5 Å, $m/m_H = 1$–20) at a fixed barrier height. The low-temperature rate constant may thus extend over the entire region of experimentally accessible values. Several one-dimensional models of tunneling are presented in more detail in Chapter 3 of this volume.

Experimental studies of a large number of low-temperature solid-phase reactions undertaken by many groups in the 1970s and 1980s have confirmed the two basic predictions of Goldanskii's model for $k(T)$: the existence of a low-temperature limit k_c and a characteristic crossover temperature T_c. The aforementioned difference between quantum chemical reactions and the classical ones has also been found, namely the values of k_c for different systems range over many orders of magnitude, even for reactions with similar values of V_0 and thus with similar Arrhenius behaviors. For illustration, a number of typical experimental $k(T)$ dependencies is represented in Figure 1.1.

At $T < T_c$ tunneling manifests itself not only in irreversible chemical reactions, but also in spectroscopic splittings. Tunneling breaks the degeneracy of symmetric potential wells and gives rise to tunnelling multiplets that can be detected by a variety of spectroscopic techniques, from inelastic neutron scattering to optical and microwave spectroscopy.

The most illustrative examples of this sort are the tunneling inversion of NH_3 and rotations of methyl groups in organic molecules. In these cases it is impossible to prepare an initial nonstationary state; that is, one cannot talk about reactants and products. Rather, the coherent tunneling motion through the barriers introduces tunneling splittings Δ in the spectra that typically range from 10^{-5} to $10^2\,cm^{-1}$ ($3 \times 10^5 - 3 \times 10^{12}\,s^{-1}$). Surprisingly, they can be measured at temperatures where the thermal energy is several orders greater than Δ. At $T > T_c$ tunneling splittings are not detected because over-barrier transitions from thermally activated energy levels at $E > V_0$ effectively compete with tunneling, and thereby destroy the coherence of the motion between potential wells.

In nearly all cases, the values of k_c and T_c derived from the experimental curves $k(T)$ are not in agreement with one-dimensional tunneling calculations that utilize crystallographic and spectroscopic data to define the tunneling distance d. Furthermore, in stark contrast to the

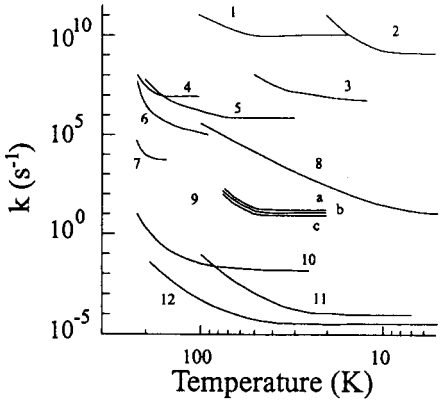


Figure 1.1 Examples of temperature dependences of rate constants for the reactions in which the low-temperature rate constant limit has been observed; 1, hydrogen transfer in excited singlet state of molecule (6.14); 2, molecular reorientation in methane crystal; 3, internal rotation of CH_3 group in radical (7.42); 4, inversion of oxyranyl radical (8.18); 5, hydrogen transfer in the excited triplet state of molecule (6.20); 6, isomerization in the excited triplet state of molecule (6.22); 7, tautomerization in the ground state of 7-azoindole dimer (6.15); 8, polymerization of formaldehyde; 9, limiting stage of chain (a) hydrobromination, (b) chlorination, and (c) bromination of ethylene; 10, isomerization of sterically hindered aryl radical (6.44); 11, abstraction of a hydrogen atom by methyl radical from a methanol matrix in reaction (6.41); 12, radical pair isomerization in dimethylglyoxime crystal (Figure 6.25).

prediction of Eq. (1.6), the crossover temperature T_c was found to have only a weak dependence on the mass of the tunneling particle. The key to understanding this behavior is in realizing that the PES of even the simplest chemical reaction is multidimensional (the dimensionality $N \geq 2$), and the potential barrier $V(Q)$ defines a saddle point that represents a maximum along Q but a minimum on the $(N-1)$-dimensional surface dividing the reactant and product valleys. Reduction of the N-dimensional reaction surface to a level that is mathematically and/or computationally tractable remains a significant challenge for theorists. A discussion of general strategies for reducing the dimensionality of the reactive surface is presented in the second section of this chapter.

In general, all the N degrees of freedom participate in the classical motion of the system, which involves, in particular, low-frequency modes such as intermolecular phonon and libron modes. These modes may be especially important when an atom or fragment is transferred between molecules in neighboring lattice sites. When the frequencies of these vibrations ω are less than $\omega_{\#}$, the Arrhenius dependence extends into the region where $T < T_c$ (albeit with smaller E_a) until these vibrations freeze

out at $k_B T < \hbar\omega/2$, or until the low-frequency vibrations cease to participate in the transition.

In the first case the crossover temperature is given by

$$k_B T_c' = \frac{\hbar\omega}{2} < k_B T_c \tag{1.9}$$

and is not connected with $\omega_{\#}$ at all. In the second case where the low-frequency modes decouple from the reaction, the tunneling trajectories should differ from the classical ones in that they do not pass through the saddle point. Consequently, the height of the barrier through which the particle tunnels is actually greater than that for the classical transition. Both effects show up in tunneling reactions and this explains in part why k_c and T_c differ from the values calculated within one-dimensional static-barrier models.

The recognition of these shortcomings of the one-dimensional models has spurred the development of new multidimensional models in which the reactant motion creates a dynamic barrier that has qualitatively different characteristics compared with the static barrier. A simple dynamical model of low-temperature tunneling reactions, referred to as the *fluctuational barrier preparation* model (or *vibration-assisted tunneling*) was introduced in the early 1980s [Benderskii et al., 1980; Ovchinnikova, 1979; Trakhtenberg et al., 1982]. Only more recently has the close relationship of this model to the contemporary quantum transition state theory (QTST) been recognized. The continuing development of QTST since the 1970s [Babamov and Marcus, 1981; Miller, 1974; 1983; Truhlar and Kuppermann, 1971] has stimulated both theoretical and experimental studies of quantum chemical reactions. Because these reactions, unlike the classical ones, correspond to small transition probabilities and are observed in the absence of thermal activation, many of the early results of low-temperature reactions that went almost unnoticed have at last been thrust into the mainstream of development of fundamental concepts in chemical kinetics. Advances in quantum chemical dynamics during the past decade now permit unified descriptions of such seemingly disparate phenomena as spectroscopic tunneling splitting (with transition frequencies 10^{10}–$10^{11}\,s^{-1}$) and slow low-temperature chemical conversions (with rate constants as slow as $10^{-5}\,s^{-1}$).

Computations have shown that in the quantum temperature regime, different most probable transition paths (ranging from the classical minimum energy path (MEP) to the straightforward one-dimensional tunneling of early models) are possible, depending on the geometry of the potential energy surface (PES). Several extensions of the one-dimension-

al models to two and higher dimensions are discussed in Chapters 4 and 5.

Quantum effects in low-temperature chemistry are discussed in the recent book by Goldanskii et al. [1989a] and in reviews by Jortner and Pullman [1986], Goldanskii et al. [1989b], and Benderskii and Goldanskii [1992]. The analyses of a limited number of solid-state reactions given in the book and reviews are based on the theory of radiationless transitions [Kubo and Toyazawa, 1955], which was developed for studies of optical properties of impurity centers in crystals. These do not reflect the sweeping progress in the general quantum theory of chemical reactions. Most of the early applications of QTST were in the area of gas-phase chemical reactions, though quantum effects are not usually dominant here because of the relatively high interaction energies required by the experimental techniques. However, modern quantum theory holds great promise for examining the dynamics of low-temperature reactions, which in turn provide fertile ground for testing this theory.

Much of the experimental results in the area of low-temperature chemical reactions are collected in the review by Benderskii and Goldanskii [1992], but the spectroscopic manifestations of tunneling are not considered in detail. Nevertheless, high-resolution spectroscopy, in combination with supersonic cooling, provides unique opportunities for studying tunneling in isolated molecules and dimers at extremely low temperatures. The simplicity of these gas-phase systems in comparison with solids permits the description of tunneling effects at a higher quantitative level, thereby expanding our understanding in this field. In this volume we consider contributions of both gas-phase and condensed-phase experiments to contemporary low-temperature dynamics in a unified approach. The results of spectroscopic and kinetic studies are compared with theoretical calculations using several different types of models and levels of sophistication. In each case, the objective is to determine the true nature of the transition dynamics as $T \to 0$.

1.2. THE ROUTES OF SIMPLIFYING THE PROBLEM

The central problem of elementary chemical reaction dynamics in condensed phases is to find the rate constant of transition in the reaction complex interacting with its environment. This problem is closely related to the more general problem of statistical mechanics of irreversible processes (see, e.g., Blum [1981] and Kubo et al. [1985] for a treatment of relaxation of an initially nonequilibrium state of a particle in the presence of a heat reservoir). If the particle is coupled to the reservoir weakly enough, then the properties of the latter are fully determined by

the spectral characteristics of its susceptibility coefficients. Moreover, in this linear response (weak coupling) limit any reservoir may be thought of as an infinite number of oscillators $\{q_j\}$ with an appropriately chosen spectral density, each coupled linearly in q_j to the particle coordinates. The coordinates q_j may not have a direct physical sense; they may be just unobservable variables whose role is to provide the correct response properties of the reservoir.

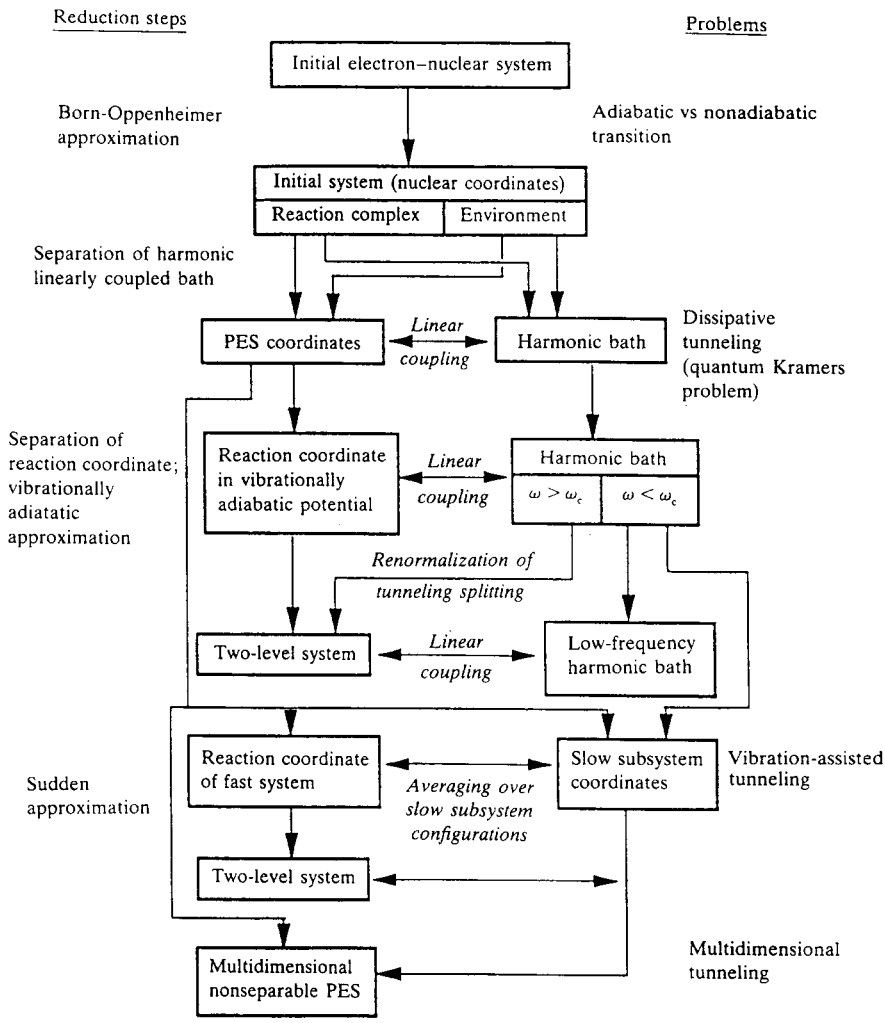
In a chemical reaction the role of a particle is played by the reaction complex, which itself includes many degrees of freedom. Therefore, the separation of reservoir and particle does not suffice for making the problem tractable, and the successive reduction of internal degrees of freedom in the reaction complex is required. Several possible ways to accomplish such a reduction are summarized in Table 1.1.

By convention, we divide the total system characterized by nuclear coordinates and composed of reactant complex and environment into the PES coordinates and the heat bath, by using the weak coupling criterion. Thus, the set of PES coordinates will not in general be identical to the reactant complex because it contains only those degrees of freedom that cannot be separated and put into the harmonic heat bath because of their strong coupling to the reaction coordinate. Because the calculation of any multidimensional PES is a difficult and time-consuming task, in most cases the choice of the internal PES coordinates is based on models that take into account information about the structure, barrier height, and characteristic frequencies of the reaction complex and its environment.

In most cases the consideration of low-temperature chemical reactions is, for practical purposes, restricted to a single PES. However, in general, a chemical reaction is a passage between two (or several) electronic states, each characterized by its own PES (reactant and product *diabatic terms*). Interaction between these states (*diabatic coupling*) often causes the states to avoid each other and creates two new adiabatic PES's, one of which (the lower) connects the reactant and product states in a continuous way. The upper and lower surfaces are separated by the adiabatic splitting, which is a measure of the strength of interaction between the zero-order diabatic terms. For low-temperature chemical reactions, the usual case is that the adiabatic splitting is large. Tunneling occurs through a barrier on a single adiabatic surface, and the role of nonadiabaticity is to modify the preexponential factor.

Once an adiabatic potential energy surface has been defined, the next step is to determine the minimum energy path (MEP). Within the

TABLE 1.1
Reduction of the General Quantum Dynamics Problem



vibrationally adiabatic approximation, high-frequency modes will, in general, be effectively decoupled from the reaction so that motion along these coordinates preserves the respective quantum numbers (usually $n = 0$). Specifically, by separating degrees of freedom having frequencies

ω_j that are greater than ω_0 (and $\omega_\#$), a vibrationally adiabatic potential [Miller, 1983] can be introduced, viz.,

$$V_{\mathrm{vad}}(Q) = V(Q) + \sum_j \frac{\hbar\omega_j(Q)}{2} \tag{1.10}$$

If all the PES coordinates are split off in this way, the original multi-dimensional problem reduces to that of one-dimensional tunneling in the effective barrier (1.10) of a particle that is coupled to the heat bath. This problem is known as the dissipative tunneling problem, which has been a topic of intense study for the past 15 years primarily in connection with tunneling phenomena in solid state physics [Caldeira and Leggett, 1983]. Interaction with the heat bath leads to a friction force that acts on the particle moving in the one-dimensional potential (1.10). As a consequence, the barrier frequency $\omega_\#$ is replaced by the Kramers' frequency $\lambda_\#$ [Kramers, 1940] defined by

$$\lambda_\# = \omega_\# \left\{ \left[1 + \left(\frac{\eta}{2\omega_\#} \right)^2 \right]^{1/2} - \frac{\eta}{2\omega_\#} \right\} \tag{1.11}$$

where η is the friction coefficient. According to Hanggi [1986] and Hanggi et al. [1990], the crossover temperature decreases to

$$k_{\mathrm{B}} T_{\mathrm{c}} = \frac{\hbar\lambda_\#}{2\pi} \tag{1.12}$$

For CLTST to be valid, the friction should maintain thermal equilibrium in the initial state without significantly affecting the transition rate for over-barrier trajectories. Therefore, in addition to the conditions in Eq. (1.1), we impose the additional requirement

$$(\beta V_0)^{-1} < \frac{\eta}{2\omega_\#} < 1 \tag{1.13}$$

At low temperatures ($\beta\hbar\omega_0 \gg 1$) only the lowest initial eigenstate actually participates in the transition, and the problem permits a further reduction to a two-level system (TLS) [Leggett et al., 1987; Suarez and Silbey, 1991b]. In doing so, one separates the high-frequency part of the bath spectrum (vibrations with frequencies $\omega > \omega_{\mathrm{c}}$ where ω_{c} is a characteristic cutoff frequency). The tunneling is considered instantaneous on the time scale of the low-frequency bath vibrations ($\omega < \omega_{\mathrm{c}}$) and thus is described by a tunneling matrix element Δ, which is renormalized by the high-frequency vibrations [Leggett et al., 1987]. In essence, the rate theory version based on the model of a TLS coupled to a low-frequency heat

bath is a golden rule approach that utilizes the basic formula

$$k = \frac{2\pi}{\hbar}\left(\frac{\Delta}{2}\right)^2 \rho_f \mathrm{FC} \tag{1.14}$$

where $\Delta/2$ is the tunneling matrix element (half the tunneling splitting in the isolated TLS), ρ_f is the density of energy levels in the final state, and FC is the Franck-Condon factor (i.e., the square of the overlap integral of oscillator wave functions for the initial and final states).

With this model it is possible to relate the frequency spectrum of the bath to the temperature dependence of the rate constant. For a bath of classical oscillators ($\beta\hbar\omega_c \ll 1$) the Franck-Condon factor is proportional to $\exp(-\beta E_r/4)$, where the reorganization energy E_r is given by

$$E_r = \frac{1}{2}\sum m_j \omega_j^2 \, \Delta q_j^2 \tag{1.15}$$

and Δq_j is the shift of the jth oscillator associated with transition. The heat bath reorganization therefore contributes an amount $V_0 = E_r/4$ to the barrier.

At low temperatures ($\beta\hbar\omega_c \gg 1$) the contributions from one-phonon, two-phonon processes, etc., can be systematically extracted from the general expression for the rate constant, and the type of the dominant process is determined by the bath spectrum and temperature. The results of Leggett et al. [1987] show that quantum dynamics of a TLS crucially depends on the spectrum of the bath. For sufficiently strong coupling, the bath may dramatically slow the tunneling rate, even to the point of localizing the particle in one of the wells. This strong dependence on the bath spectrum is inherent to the quantum dynamics and does not show up in classical transitions.

Whereas the reorganization energy of the bath modes may slow the tunneling rate by raising the effective barrier, there are other modes that may be efficient promoters of the tunneling by lowering the barrier and/or by reducing the tunneling distance. The dissipative tunneling model, as it is formulated in Leggett et al. [1987], does not properly account for these "promoting" vibrational modes, which are strongly coupled to the particle and do not belong to the heat bath in the above weak coupling sense. Consider, for example, tunneling of a hydrogen atom in an OH$\cdots$O fragment, as illustrated in Figure 1.2. The height and width of the barrier for the H atom depends on the O–O distance. On the other hand, the O–O distance is the same in the initial and final states, i.e., the reorganization energy corresponding with the O–O vibration equals zero. If the promoting vibration has a high frequency, it

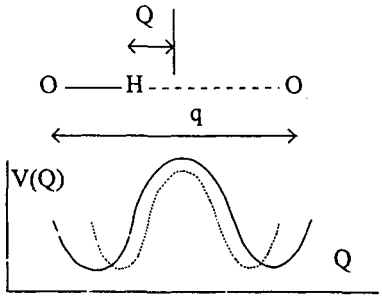


Figure 1.2. Transfer of the hydrogen atom in the linear OH···O fragment promoted by stretching O–O vibration. The solid curve corresponds to the equilibrium O–O distance, $q = q_0$; the dotted curve corresponds to $q < q_0$.

can be incorporated by using the vibrationally adiabatic potential along the MEP (1.10). On the other hand, if the promoting mode has a very low frequency, then tunneling occurs instantaneously on the time scale of promoting vibrations of the heavy fragments, and its rate results from averaging over the slow subsystem configurations [Benderskii et al., 1980; Ovchinnikova, 1979; Trakhtenberg et al., 1982]. The most probable tunneling path in this case differs from the MEP. This idea, later christened the sudden approximation, has recently been developed in detail by Levine et al. [1989] in connection with dissipative tunneling within the framework of quantum transition state theory. Following Siebrand et al. [1984], Suarez and Silbey [1991b], and Borgis et al. [1989], the promoting vibrations (q_p) are incorporated into the TLS model by introducing the tunneling matrix element dependence

$$\Delta = \Delta_0 \exp(-\gamma q_p) \tag{1.16}$$

where γ^{-1} is small compared to the tunneling distance. For OH···O fragments the value of γ^{-1} is in the range 0.03–0.04 Å [Borgis et al., 1989].

In realistic systems the separation of the modes by their frequencies and subsequent reduction to one dimension with the methods described above is often not possible. In this case an accurate multidimensional analysis is needed. Another case in which a multidimensional study is required and which obviously cannot be accounted for within the dissipative tunneling model is that of a complex PES with several saddle points and therefore several MEPs and tunneling paths. Whereas the goal of the previous models is to carry out analytical calculations and gain insight into the physical picture, the multidimensional calculations are expected to give a quantitative description of concrete chemical systems. However, at present we are just at the beginning of this process, and only a few examples of numerical multidimensional computations, mostly on rather idealized PES's, have been performed so far. Nonetheless, these