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DIFFUSION THEORY OF REACTION RATES. I. FORMULATION AND EINSTEIN--ETC(U)

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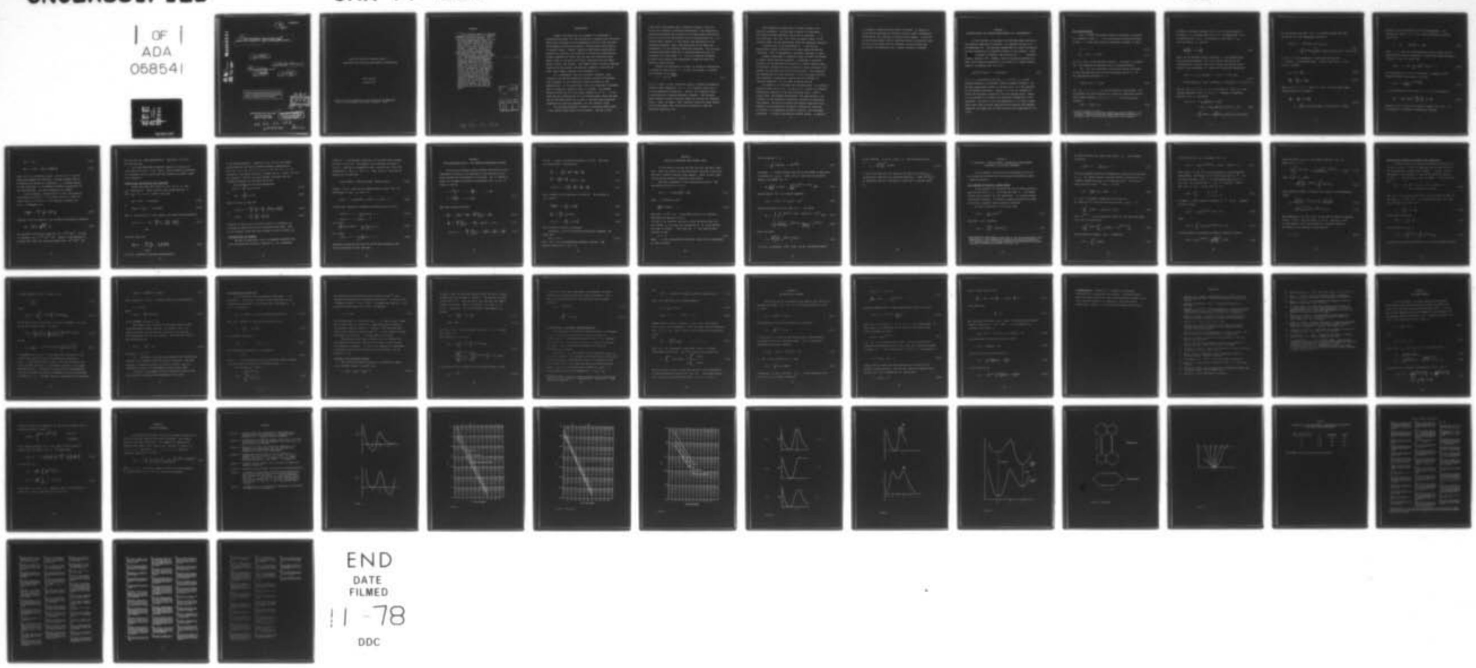

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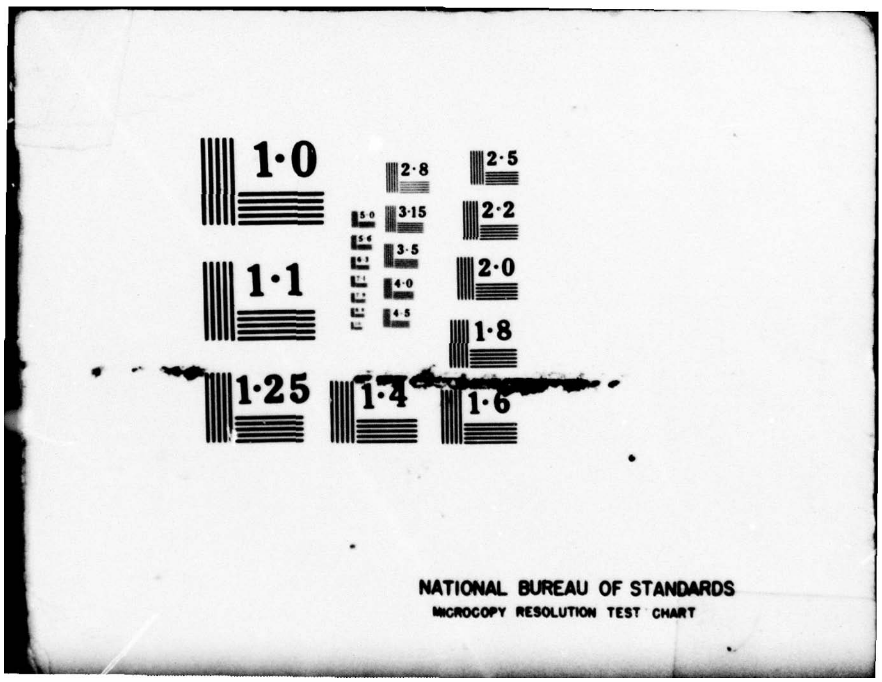
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DIFFUSION THEORY OF REACTION RATES, I: FORMULATION AND EINSTEIN – SMOLUCHOWSKI APPROXIMATION

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DIFFUSION THEORY OF REACTION RATES, I:

FORMULATION AND EINSTEIN-SMOLUCHOWSKI APPROXIMATION

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ABSTRACT

The diffusion model of reaction rates, originally due to H. Kramers, is rederived and extended. The derivation follows the work of Il'in and Khasminskii and is based on a clear physical picture of the molecular events. The origin of the stochastic forces is also clearly treated. Classical mechanics is used throughout. ~~In~~ this paper, ~~we~~ uses the Einstein-Smoluchowski approximation and, thus, considers a diffusion model in position space only. ~~We non-dimensionalize~~ the diffusion equations * and ~~obtain~~ a number of singular perturbation problems are obtained. By using the diffusion model, one can treat a number of problems involving reaction rate theory. ~~We derive~~ a new form of transition state theory is derived. ~~We~~ calculate reaction rate constants, transmission coefficients and the lifetime of the activated complex are calculated. Kramers' result is the leading term in the asymptotic expansion of the rate constant that we calculate. We show how absorption spectra can also be derived by use of the diffusion model.

* is nondemensionalized

INTRODUCTION

Almost forty years ago, H.A. Kramers (1) introduced a Brownian motion model for the calculation of reaction rate constants. The picture involved in this formulation is one in which the molecules undergo a diffusion process in reaction space while moving in physical space. Kramers' theory is particularly applicable to reactions in solution, and reactions of relatively large molecule. Kramers compared his theory with the then new transition state theory (TST) or activated rate theory associated with the names Wigner, Eyring, and Polayni. The Kramers theory has been relatively unnoticed by the chemical and physical community, while TST and other, more complex theories have developed (2).

As a consequence, there are excellent classical, semiclassical, and quantum mechanical methods available to calculate rate constants for the reactions of small molecules in the gaseous phase. On the other hand, when large molecules or polymers react in solution a complete theory is lacking. The Kramers diffusion model can fill this gap(an example is in (3)). In this paper and the following one (4), we extend Kramers theory and show how the diffusion model can be used to calculate many properties connected with reaction phenomena, not just reaction rates.

The diffusion approach is based on a Brownian motion model in the reaction phase space of the molecule. The use of such phase space distributions was initiated by Wigner in 1932 (5). By the use of Wigner's technique coefficients in the differential equations describing the evolution of the phase space distribution function can be given approximate quantum interpretations (6). Our interest here, however, is the solution and application of the diffusion equations, rather than derivation of the equations. Consequently, we use classical mechanics throughout. The extension to Wigner equivalent formalism is straightforward and will be considered in a later paper (7). By using classical mechanics, we also use an implicit Born-Oppenheimer assumption about the potential energy surface.

Kramers was motivated by a desire to develop an alternative to transition state theory (1). In TST, one obtains a reaction rate constant of the form:

$$k = \kappa(f\cdot f\cdot)e^{-Q/k_B T} \tag{1.1}$$

In (1.1), $Q/k_B T$ is the "activation energy" divided by Boltzmann's constant times temperature, $(f\cdot f^{\cdot})$ is a frequency factor and κ is the transmission coefficient. Usually, the frequency factor is calculated by a quantum mechanical argument. The diffusion model provides a purely classical method of treating the frequency factor. Hence, we obtain CTST, classical transition state theory. CTST and TST agree, when the partition functions in TST are calculated explicitly (8).

The transmission coefficient is usually treated as an empirical parameter. TST provides no method of calculating κ. The diffusion model provides a direct way to calculate κ. We will show that TST and CTST arise as special cases, of the diffusion model (in the equilibrium limit and vanishing viscosity).

Previous work on the calculation of κ was done by Hirschfelder, Wigner and Hulburt (24) using quantum mechanical techniques. Here a complementary, stochastic approach is given.

Kramers constructed a stochastic model and used the forward or Fokker-Planck diffusion equation. He managed to construct solutions of the Fokker-Planck equation in certain special cases. The deviation between TST and the diffusion theory was about 10-15 percent for reactions with high energy barriers. The difference was considerable for lower barriers. We will calculate reaction rate constants, transmission coefficients and lifetimes of activated complexes, for all sizes of energy barrier.

In section 2, we introduce the diffusion model. Our analysis closely follows that in (9). We are led to a system of stochastic differential equations in the reaction phase space. Under a second limit, the Einstein-Smoluchowski (ES) approximation, the structure of the stochastic differential equation is simplified considerably. We give the forward and backward equations corresponding to both systems of stochastic differential equations. In section 3, the equations derived in section 2 are non-dimensionalized. A singular perturbation problem arises. In section

4, classical transition state theory is derived. In section 5, we use the ES equations to calculate reaction rates, transmission coefficients, and lifetimes of the activated complex. In section 6, we show how spectra can be calculated using the diffusion model. Not all of our results are new; however, we are unifying many old results and questions with a simple conceptual framework.

SECTION 2

DIFFUSION MODEL AND EINSTEIN-SMOLUCHOWSKI (ES) APPROXIMATION

In this section, we introduce the diffusion model and derive the diffusion equations of interest. Our approach follows Il'in and Khasminski (9). The physical assumptions are clearly delineated and the introduction of stochastic effects is also obvious. Since the model is based on dynamics, one could use the projector operator approach (10). However, when the projection operator is used, the stochastic assumption is introduced in a hidden fashion, usually, by assuming that (e.g.,(11))

$$\langle A(t)e^{iL_o t} B(t)\rangle = \langle A(t)\rangle\langle B(t)\rangle \tag{2.1}$$

if $t > \tau_c$, for some cut off time τ_c. In(2.1) L_o is the Liouville operator, and brackets indicate ensemble averages. For the very complicated systems of interest here, it is not possible to use dynamics completely. Namely, it is not yet possible to derive the stochastic properties from the dynamics alone. Hence, it is reasonable to introduce the stochastic assumptions at the beginning. The work of Il'in and Khasminskii (9) is such a model. Since their paper has gone unnoticed by the physical and chemical community, we repeat part of their analysis here (equations 2.4 to 2.16).

THE DIFFUSION MODEL

Let x denote the generic reaction coordinate of interest in a molecule of mass m . If no collisions with bath molecules, of mass μ , occur then classical mechanics is obeyed, so that*

$$\dot{x} = v \tag{2.2}$$

$$m\dot{v} = F(x) = -\nabla V(x) \tag{2.3}$$

In (2.3), V(x) is the potential function. In figure 1, we sketch V(x) for dissociation reactions and for tautomerizations.

Let $\xi(t)$ be a stochastic process that counts collisions of the large molecule with the bath molecules and let F_ξ be the distribution function of ξ :

$$\Pr\{\xi(t) \leq N\} = F_\xi(N) \tag{2.4}$$

Let $\{\tau_i\}$ i = 1, 2, ... be the jump points of the process $\xi(t)$. We represent the bath molecules by a family of identically distributed random variables $\{\Sigma_k\}$, k = 1, 2, ... with distribution function

$$R(y) = \Pr\{\Sigma_k \leq y\} \tag{2.5}$$

*For the purposes of conceptual simplicity, we will treat x as a scalar. The results of this paper immediately generalize to the vector case; by replacing integrals by line integrals.

Introduce a stochastic process $(\tilde{x}_\mu(t), \tilde{v}_\mu(t))$, which except at the points τ_k, coincides with (2.2, 2.3). We assume that $\tilde{x}_\mu(t)$ is continuous and $\tilde{v}_\mu(t)$ is continuous at the right at τ_k, with the jump at τ_k given by

$$\frac{2\mu}{m+\mu}\left[\Sigma_k - \tilde{v}_\mu(\tau_k^-)\right]. \tag{2.6}$$

Hence, we are assuming elastic collisions. If we consider more than one space dimension, then (2.6) must be modified by the introduction of a factor taking into account the spatial distribution of the collisions (4). Define the transition probability

$$\begin{aligned} P_\mu(x, \mu, t, x_1, v_1)dx_1dv_1 &\equiv P_\mu(x, v, t, dx_1, dv_1) \\ &\equiv \Pr\{\tilde{x}_\mu(t)\in(x_1,x_1 + dx_1), \tilde{v}_\mu(t)\in(v_1,v_1 + dv_1)\,|\,\tilde{x}_\mu(o) = x, \tilde{v}_\mu(o) = v\} \end{aligned} \tag{2.7}$$

Now let $\bar{x}(x, v, t)$, $\bar{v}(x, v, t)$ be solutions of (2.2, 2.3) with initial conditions $\bar{x}(o) = x$, $\bar{v}(o) = v$. Consider a integrable function $f(x, y)$ and define

$$\begin{aligned} u(x, y, t) &= E_{x,v}\left(f(\tilde{x}_\mu(t), \tilde{v}_\mu(t)\right) \\ &= \Pr\{\tau_1 > t\}E_{x,v}\left[f(\tilde{x}_\mu(t),\tilde{v}_\mu(t))\,|\,\tau_1 > t\right] \\ &\quad + \int_0^t d\Pr\{\tau_1 < S\}\int_{-\infty}^{\infty} dR(z)E_{x,v}\left[f(\tilde{x}_\mu,\tilde{v}_\mu)\,|\,\tau_1=S,\Sigma_1=z\right] \end{aligned} \tag{2.8}$$

For the special case that $\xi(t)$ is a Poisson process (the case treated by Il'in and Khasminskii) we obtain

$$
\begin{aligned}
u(x,y,t) &= e^{-at} f(\bar{x}(x,v,t),\bar{v}(x,v,t)) \\
&\quad + \int_0^t ae^{-aS} dS \int_{-\infty}^{\infty} dR(z)\; u\{\bar{x}(x,v,S),\bar{v}(x,v,S) + \nu(z-\bar{v}),t-S\}
\end{aligned}
\tag{2.9}
$$

In (2.9), a is the parameter of the Poisson process and $\nu = 2\mu/(m+\mu)$ is the reduced mass. We note that $\bar{x}(x,v,t)$ and $\bar{v}(x,v,t)$ satisfy

$$y_t - vy_x - \frac{F}{m} y_v = 0 \tag{2.10}$$

$$\frac{dy}{dt} = \frac{dx}{dt} y_x + \frac{dv}{dt} y_v \tag{2.11}$$

where $y = \bar{x}$ or $y = \bar{v}$. Thus, if $f(x,v)$, $F(x)$ are three times differentiable (2.9) becomes:

$$
\begin{aligned}
\frac{\partial u}{\partial t} &= v\frac{\partial u}{\partial x} + F(x)\frac{\partial u}{\partial v} \\
&\quad + a \int_{-\infty}^{\infty} u(x,v+\nu(z-y),t)\,dR(z); \text{ with } u(x,y,o) = f(x,y)
\end{aligned}
\tag{2.12}
$$

Equation (2.12) was derived by Il'in and Khasminskii. Now consider the limit $a >> 1$ (i.e., many collisions per second). Then we set

$$a\mu = \frac{\eta}{2} \qquad E_{\Sigma}[\mu\Sigma_k^2] = k_B T \tag{2.13}$$

where η, T have the interpretations of the viscosity of the medium and the absolute temperature, respectively (where Boltzmann's constant is k_B). We assume that

$$E_R(z) = 0 \quad \text{and} \quad \lim_{\mu\to 0} \mu^2 \int |z|^3 \, dR_\mu(z) = 0 \tag{2.14}$$

The assumptions in (2.14) are satisfied, for example, by the Maxwell Boltzmann distribution, for which

$$R_\mu(z) = \sqrt{\frac{\mu}{2\pi k_B T}} \; e^{-\mu z^2/2k_B T} . \tag{2.15}$$

Il'in and Khasminskii prove that as $\mu \to 0$ (2.12) converges to

$$\frac{\partial u}{\partial t} = v \frac{\partial u}{\partial x} + \frac{F}{m}\frac{\partial u}{\partial v} + \frac{\eta T k_B}{m^2}\frac{\partial^2 u}{\partial v^2} - \frac{\eta}{m} v \frac{\partial u}{\partial v} \tag{2.16}$$

Equation (2.16) is exact and rigorous (compare with (12)). It corresponds to a stochastic differential equation

$$d\tilde{x} = \tilde{v}\, dt \tag{2.17}$$

$$m d\tilde{v} = (F(\tilde{x}) - \eta\tilde{v})dt + \sqrt{2k_B T\eta}\, dW \tag{2.18}$$

where $W(t)$ is the Wiener process. We call 2.16 - 2.18 the Ornstein-Uhlenbeck (OU) equations. We have obtained them by introducing two stochastic assumptions: 1) a Poisson process for the collisions; 2) the Maxwell Boltzmann distribution for the bath molecules. No other assumptions are needed.

We now consider a second limit of (2.16), the Einstein-Smoluchowski or ES limit. In the limit that $m/\eta \to 0$ (high viscosity) with F/η non-zero, (2.16) becomes an equation for $u(x,t)$; independent of v:

$$\frac{\partial u(x,t)}{\partial t} = \frac{k_B T}{\eta} \frac{\partial^2 u}{\partial x^2} + \frac{F(x)}{\eta} \frac{\partial u}{\partial x} \tag{2.19}$$

Equation (2.19) corresponds to the stochastic differential equation

$$d\tilde{x} = \frac{F(\tilde{x})}{\eta} dt + \sqrt{\frac{2k_B T}{\eta}}\, dW \tag{2.20}$$

For molecules of molecular weight 50, $m/\eta \sim 10^{-12}$ $\sec^{-1}$ (13) and for polymers $m/\eta \sim 10^{-13}$ $\sec^{-1}$ (10). Hence, if the reactions of interest have rates that are much greater than 10^{-12} $\sec^{-1}$, the

ES limit will be a good approximation. Physically, this will often be the case.

Il'in and Khasminskii construct asymptotic solutions of (2.16) and (2.17) for $\varepsilon = m/\eta$ small. Here we shall be interested in a different type of scaling and will construct different asymptotic solutions.

FOKKER-PLANCK AND EXPECTED TIME EQUATIONS

Denote the right hand sides of (2.16, 19) by Lu and $L_{ES}u$ respectively. These operators have formal adjoints L^* and L^*_{ES}. Let p be a function such that

$$pLu - uL^*p = \text{divergence} \tag{2.21}$$

or

$$pL_{ES}u - uL^*_{ES}p = \text{divergence} \tag{2.22}$$

Then p will satisfy, at least weakly, the Fokker-Planck equations:

$$p_t(x,v,t) = -vp_x + \frac{\eta k_B T}{m^2} p_{vv} - \left[\left(\frac{F}{m} - \frac{\eta v}{m}\right)p\right]_v \tag{2.23}$$

$$\equiv L^*p$$

in the OU case, and

$$\frac{\partial p}{\partial t}(x,t) = \frac{k_B T}{\eta} \frac{\partial^2 p}{\partial x^2} - \frac{\partial}{\partial x}\left(\frac{F(x)p}{\eta}\right) \tag{2.24}$$

$$\equiv L^*_{ES}p$$

In (2.23) a subscript indicates differentiation.

in the ES approximation. Equations (2.23, 24) are the Fokker-Planck equations and hold if certain boundary conditions are met (e.g., $p \to 0$ as $x^2 + v^2 \to \infty$, $u \to 0$ as $x^2 + v^2 \to \infty$). No expansion of the master equation is needed (12,13). Since (2.16,19) are rigorous, (2.23,24) are also rigorous, provided that the boundary conditions are satisfied (14,15,16).

Now consider the following definitions

$$\bar{t}(x,v) = \int_0^\infty t u_t(x,v,t)dt \qquad (2.25)$$

or

$$\bar{t}(x) = \int_0^\infty t u_t(x,t)dt \qquad (2.26)$$

Then it is easy to show that

$$-u(x,v,\infty) = \frac{k_B T\eta}{m^2}\frac{\partial^2 \bar{t}}{\partial v^2} + \frac{v\partial\bar{t}}{\partial x} + \left(\frac{F(x) - \eta v}{m}\right)\frac{\partial\bar{t}}{\partial v} \qquad (2.28)$$

or

$$-u(x,\infty) = \frac{k_B T}{\eta}\frac{\partial^2 \bar{t}}{\partial x^2} + \frac{F(x)}{\eta}\frac{\partial\bar{t}}{\partial x} \qquad (2.29)$$

Equations (2.28,29) were derived by Klein (17) and Weiss (18) by different means and solved in some particular cases. None of the problems solved here were treated by Klein or Weiss (19).

INTERPRETATIONS AND REMARKS

We have not specified $f(x,v)$ or boundary conditions for any of the equations derived in section 2.2. By a judicious choice of f and boundary conditions, we can solve many problems by using (2.16-2.25). For example, with reference to figure 1, $u(x,v,t)$ could be the probability that a particle has $\tilde{x}(t) \geq \hat{x}$, conditioned on $\tilde{x}(o) = x$, $\tilde{v}(o) = v$. Then $p(x,v,t)$ would be the density for the particle:

$$p(x,v,t)dxdv = \Pr\{\tilde{x}(t) \in (x,x+dx),\ \tilde{v}(t) \in (v,v+dv)\} \tag{2.30}$$

Finally, $\bar{t}(x,v)$ would be the expected time to reach $\tilde{x}(t) \geq \hat{x}$, conditioned on $\tilde{x}(o) = x$, $\tilde{v}(o) = v$:

$$\bar{t}(x,v) = E \min\{t : \tilde{x}(t) = \hat{x} \mid \tilde{x}(o) = x,\ \tilde{v}(o) = v\} \tag{2.31}$$

In this case, appropriate boundary conditions are for (2.16):

$$u(\hat{x},v,t) = 1, \qquad \lim_{x \to -\infty} u(x,v,t) = 0 \tag{2.32}$$

$$u(x,v,o) = 0 \quad \text{unless} \quad x = \hat{x}$$

for (2.23):

$$\iint p(x,v,t)dxdv = 1 \qquad \lim_{x^2+v^2 \to \infty} p(x,v,t) = 0 \tag{2.33}$$

for (2.28):

$$\bar{t}(\hat{x},v) = 0 \qquad \lim_{x \to -\infty} \frac{\partial \bar{t}}{\partial x}(x,v) = 0 \tag{2.34}$$

Analogous interpretations hold for the ES limit equations, and will be discussed in later sections.

SECTION 3

NON-DIMENSIONALIZATION - THE SINGULAR PERTURBATION PROBLEM

We will now introduce scaled variables and derive the non-dimensional versions of the equations in the previous section. First consider the OU equations (2.16,23,28). Let Q denote an energy (for example the height of the barrier from $\hat{x}_o$ to x in figure 1) and let

$$v = \sqrt{\frac{Q}{m}}\, v' \qquad x = \sqrt{\frac{Qm}{\eta^2}}\, x' \qquad t = \frac{m}{\eta} t'$$
$$F = \sqrt{\frac{\gamma^2 Q}{m}}\, F' \qquad W = \sqrt{\frac{m}{\gamma}}\, W' \tag{3.1}$$

Then the OU equations become

$$\frac{\partial u}{\partial t'} = v'\frac{\partial u}{\partial x'} + F'\frac{\partial u}{\partial v'} + \frac{k_B T}{Q}\frac{\partial^2 u}{\partial (v')^2} - v'\frac{\partial u}{\partial v'} \tag{3.2}$$

$$\frac{\partial p}{\partial t'} = \frac{k_B T}{Q}\frac{\partial^2 p}{\partial (v')^2} - v'\frac{\partial p}{\partial x'} - \frac{\partial}{\partial v'}[(F' - v')p] \tag{3.3}$$

$$-u(x',v',\infty) = \frac{k_B T}{Q}\frac{\partial^2 \bar{t}'}{\partial (v')^2} + F'\frac{\partial \bar{t}'}{\partial v'} + v'\frac{\partial \bar{t}'}{\partial x'} - v'\frac{\partial \bar{t}'}{\partial v'} \tag{3.4}$$

We let $\varepsilon = k_B T/Q$ and drop the primes in (3.2-4). The final non-dimensional OU equations are

$$\frac{\partial u}{\partial t} = \varepsilon \frac{\partial^2 u}{\partial v^2} + F\frac{\partial u}{\partial v} + v\frac{\partial u}{\partial x} - v\frac{\partial u}{\partial v} \tag{3.5}$$

$$\frac{\partial p}{\partial t} = \varepsilon \frac{\partial^2 p}{\partial v^2} - v\frac{\partial p}{\partial x} - \frac{\partial}{\partial v}\left[(F - v)p\right] \tag{3.6}$$

$$-u(x,v,\infty) = \varepsilon \frac{\partial^2 \bar{t}}{\partial v^2} + F\frac{\partial \bar{t}}{\partial v} + v\frac{\partial \bar{t}}{\partial x} - v\frac{\partial \bar{t}}{\partial v} \tag{3.7}$$

Next, consider the ES equations (2.19,24,29). The scalings in (3.1) lead to

$$\frac{\partial u(x,t)}{\partial t} = \varepsilon \frac{\partial^2 u}{\partial x^2} + F(x)\frac{\partial u}{\partial x} \tag{3.8}$$

$$\frac{\partial p}{\partial t} = \varepsilon \frac{\partial^2 p}{\partial x^2} - \frac{\partial}{\partial x}(F(x)p) \tag{3.9}$$

$$-u(x,\infty) = \varepsilon \frac{\partial^2 \bar{t}}{\partial x^2} + F(x)\frac{\partial \bar{t}}{\partial x} \tag{3.10}$$

Other choices of scaling are possible.

Equations (3.5-10) are singular perturbation problems. We assume that

$$F(x) = -V(x), \tag{3.11}$$

where $V(x)$ is a non-dimensional potential function. The physical potential is $V(x) \cdot Q$.

SECTION 4

CLASSICAL TRANSITION STATE THEORY (CTST)

In this section, we show how TST fits into the above framework. Since our results are derived without recourse to partition functions, Planck's constant never appears. Hence, we call these results purely classical transition state theory.

The major assumption is that equilibrium prevails. The equilibrium solution of (3.6) is

$$p(x,v) \quad = \quad c \exp[-\frac{1}{\varepsilon}(\frac{v^2}{2} + V(x))] \tag{4.1}$$

where c is chosen so that

$$\iint p(x,v)dxdv \quad = \quad 1 \tag{4.2}$$

Note that $H = \frac{v^2}{2} + V(x)$ is the Hamiltonian of the classical deterministic equations (2.2,3).

Our goal is to calculate the rate at which particles leave the well around x_o and pass over the barrier at $\hat{x}$, going towards the right in figure 1. Call this rate j. The reaction rate constant is then

$$k \quad = j\kappa \tag{4.3}$$

where κ is the transmission coefficient, which will be calculated in later sections.

The flux across $\hat{x}$ is

$$J = \int_0^\infty vp(\hat{x},v)dv = \varepsilon c e^{-V(\hat{x})/\varepsilon} \tag{4.4}$$

To obtain j, we must divide this flux by the number of particles in the well at x_o, N_o. Since $p(x,v)$ also gives the particle density, the number N_o is

$$N_o = \iint_{\text{WELL}} p(x,v)dv = \iint_{\text{WELL}} e^{-\frac{1}{\varepsilon}(v^2/2 + V(x))} dxdv \tag{4.5}$$

We now replace $V(x)$ by a Taylor expansion

$$V(x) = V(x_o) + \tfrac{1}{2} V''(x_o)(x - x_o)^2 \tag{4.6}$$

and let the limits in (4.5) tend to $\pm\infty$. We obtain

$$N_o = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\frac{1}{\varepsilon}(v^2/2 + V(x_o) + \frac{1}{2}V''(x_o)(x - x_o)^2)} dvdx \tag{4.7}$$

$$= \sqrt{\frac{2\pi\varepsilon}{2}}\sqrt{\frac{2\pi\varepsilon}{V''(x_o)}}\, e^{-V(x_o)/\varepsilon} = \frac{2\pi\varepsilon}{\sqrt{V''(x_o)}}\, e^{-V(x_o)/\varepsilon} \tag{4.8}$$

Hence, we obtain

$$j = \frac{\sqrt{V''(x_o)}}{2\pi}\, e^{-V(\hat{x})/\varepsilon}\, e^{V(x_o)/\varepsilon} \tag{4.9}$$

In (4.9), we recognize $V(\hat{x}) - V(x_o)$ as the "activation energy" of the reaction. If we set $V(x_o) = 0$, then the reaction rate is:

$$k = \kappa\sqrt{\frac{V''(x_o)}{2\pi}}\; e^{-V(\hat{x})/\varepsilon} \tag{4.10}$$

It can be verified that the usual TST (8) gives this result, if the partition functions are evaluated explicitly. Often $\sqrt{V''(x_o)/2\pi}$ is identified with the "frequency of vibration" in the well about x_o.

SECTION 5

ES EQUATIONS: REACTION RATES, TRANSMISSION COEFFICIENTS, LIFETIMES OF ACTIVATED COMPLEXES*

In this section, we show how the ES equation (3.8-3.10) can be used to calculate much of the desired information about a chemical reaction.

RATE CONSTANT BY MODIFIED KRAMERS METHOD

In this section, we calculate the rate at which particles pass from the well at x_0 to the barrier peak $\hat{x}$. Our method follows that of Miller (21) and Ludwig(16); it is more accurate than Kramers approach. In addition, Kramers derivation is based on difficult, somewhat obscure physical arguments.

We seek a solution of (3.9) of the form

$$p(x,t) = \sum_{n=0} \sigma_n(x) e^{-\lambda_n t} \quad . \tag{5.1}$$

Then each $\sigma_n(x)$ satisfies

$$-\lambda_n \sigma_n = \varepsilon \frac{\partial^2 \sigma_n}{\partial x^2} - \frac{\partial}{\partial x}(F(x)\sigma_n) \quad . \tag{5.2}$$

*The results in this section generalize to the multi-dimensional case immediately if the integrals are replaced by multiple integrals. This generalization is possible because the ES approximation yields a gradient deterministic system. Also see (19).

We shall calculate the lowest eigen value, λ_o , with boundary conditions:

$$\sigma_o(\hat{x}) = 0 \qquad \frac{\partial}{\partial x}\sigma_o(x_o) = 0 \tag{5.3}$$

The first boundary condition corresponds to absorption of particles at $\hat{x}$. The second insures a constant number of particles at x_o . (Kramers assumed this also, in a disguised form.) The rate at which particles reach $\hat{x}$ from x is then

$$j(x) = \iint t\ p_t(x,t)\,dx\,dt = \lambda_o, \tag{5.4}$$

if $\sigma_o(x)$ is properly normalized (as it must be).

We integrate (5.2) once and use the fact that $\sigma_x(x_o) = 0$:

$$-\lambda_o\int_{x_o}^{x} \sigma_o(y)dy = \varepsilon \frac{\partial}{\partial x}\sigma_o(x) + V_x\sigma_o \tag{5.5}$$

Since $e^{V(x)/\varepsilon}$ is an integrating factor for the right hand side, (5.5) can be rewritten as:

$$-\frac{\lambda_o}{\varepsilon}\int_{x_o}^{x} e^{V(S)/\varepsilon}\int_{x_o}^{S} \sigma_o(y)dydS = \sigma_o e^{V(x)/\varepsilon}\Big|_{x_o}^{x} \tag{5.6}$$

Now consider the integral $I(S)$, defined by

$$I(S) = \int_{x_o}^{S} \sigma_o(y)dy \tag{5.7}$$

In the vicinity of x_o, we expand $\sigma(y)$ as

$$\sigma_o(y) = \sigma_o(x_o)\, e^{-V(y)/\varepsilon}[1 + \varepsilon g_1(y) + \varepsilon^2 g_2(y) + \ldots] \tag{5.8}$$

where $g_k(y)$ is the k^{th} order correction to the equilibrium distribution. The density in (5.8) does not vanish at $\hat{x}$, as it must to satisfy $\sigma_o(\hat{x}) = 0$ (it does satisfy $\frac{\partial}{\partial x}\sigma_o(x_o) = 0$). Let $\theta(y)$ be a neutralizer: θ is a C^∞ function, $\Theta(\hat{x})=0$ and $\theta(y) = 1$ if y is far from $\hat{x}$, e.g.,

$$\theta(y) = \begin{cases} 0 & \text{if } y = \hat{x} \\ 1 & \text{if } y < \hat{x} - \varepsilon^n \end{cases} \tag{5.9}$$

for some n, and is smooth in between $\hat{x} - \varepsilon^n$ and $\hat{x}$. Instead of (5.8), we use

$$\sigma_o(y) = \sigma_o(x_o) e^{-V(y)/\varepsilon}\ \Theta(y) + O(\varepsilon) \tag{5.10}$$

Then

$$I(S) = \int_{x_o}^{S} \sigma_o(x_o)\theta(y) e^{-V(y)/\varepsilon}\, dy + O(\varepsilon) \tag{5.11}$$

If the integral is evaluated by Laplace's method, we obtain

$$I(S) \sim \sigma(x_o) e^{-V(x_o)/\varepsilon}\ \tfrac{1}{2}\sqrt{\frac{2\pi\varepsilon}{V''(x_o)}} + O(\sqrt{\varepsilon}). \tag{5.12}$$

Using the result (5.12) in the integral equation (5.6), we obtain, for $x = \hat{x}$

$$-\frac{\lambda_o}{\varepsilon}\int_{x_o}^{\hat{x}} e^{V(s)/\varepsilon} ds \cdot \sigma_o(x_o)\sqrt{\frac{\pi\varepsilon}{2V''(x_o)}}\, e^{-V(x_o)/\varepsilon} = -\sigma_o(x_o), \tag{5.13}$$

since $\sigma_o(\hat{x}) = 0$. Hence,

$$\lambda = \varepsilon\sqrt{\frac{2V''(x_o)}{\pi\varepsilon}}\; e^{V(x_o)/\varepsilon} \Big/ \int_{x_o}^{\hat{x}} e^{V(s)/\varepsilon} ds \tag{5.14}$$

Using Laplace's method to evaluate the integral in the denominator yields

$$\lambda_o \sim \varepsilon\sqrt{\frac{2V''(x_o)}{\pi\varepsilon}}\; e^{V(x_o)/\varepsilon}\, e^{-V(\hat{x})/\varepsilon}\sqrt{\frac{2|V''(\hat{x})|}{\pi\varepsilon}} \tag{5.15}$$

$$= \frac{2}{\pi}\sqrt{V''(x_o)\,|V''(\hat{x})|}\; e^{-V(\hat{x})/\varepsilon} e^{V(x_o)/\varepsilon} \tag{5.16}$$

when comparing (5.16) and (4.10), we see that the second "frequency factor" $|V''(\hat{x})|$ does not appear in (4.10). Equation (5.16) is also Kramers result (but derived in a different fashion). The reaction rate constant is then given by

$$k = \kappa\lambda_o \tag{5.17}$$

REACTION RATE CONSTANT BY EXPECTED TIME FORMULATION

In this section, we present an alternative formulation for the rate constant. It has the advantage that we avoid having to use the asymptotic analysis which assumed $\varepsilon = k_B T/Q$ is small. Consequently, the technique of this section works for moderate or large ε (low barriers) as well as small ε (high barriers).

Let

$$\bar{t}(x) = E\{t: \tilde{x}(t) = \hat{x}, \tilde{x}(s) < \hat{x}, s < t | \tilde{x}(o) = x, \\ \tilde{x}(t) \text{ eventually crosses } \hat{x}\} \tag{5.18}$$

The $\bar{t}(x)$ is the average time that a particle takes to reach $\hat{x}$, starting at x. Then, $\bar{t}(x)$ will satisfy equation (3.10) with the left hand side equal to -1:

$$-1 = \varepsilon \frac{\partial^2 \bar{t}}{\partial x^2} + F(x) \frac{\partial \bar{t}}{\partial x} \tag{5.19}$$

and boundary conditions

$$\bar{t}(\hat{x}) = 0 \quad \lim_{x \to -\infty} \frac{\partial \bar{t}}{\partial x} = 0 \tag{5.20}$$

The solution of (5.19) is

$$t(x) = \frac{1}{\varepsilon} \int_x^{\hat{x}} e^{V(S)/\varepsilon} \int_{-\infty}^{S} e^{-V(y)/\varepsilon} dy dS \tag{5.21}$$

Following the analysis in section 5.1, we could identify the rate at which molecules reach $\hat{x}$ from x_o as

$$\lambda = \frac{1}{\bar{t}(x_o)} \tag{5.22}$$

where,

$$\bar{t}(x_o) = \frac{1}{\varepsilon} \int_{x_o}^{\hat{x}} e^{V(S)/\varepsilon} \int_{-\infty}^{S} e^{-V(y)/\varepsilon} dydS \tag{5.23}$$

To see that (5.22) is equivalent to (5.16), we assume $\varepsilon \ll 1$ and use Laplace's method twice. We obtain

$$\bar{t}(x_o) \sim \frac{1}{\varepsilon}\left[\sqrt{\frac{\pi\varepsilon}{2|V''(\hat{x})|}}\right]\left[\sqrt{\frac{\pi\varepsilon}{2|V''(x_o)|}}\right] e^{V(\hat{x})/\varepsilon} e^{-V(x_o)/\varepsilon} \tag{5.24}$$

so that

$$\lambda_o = \frac{1}{\bar{t}(x_o)} = e^{-V(\hat{x})/\varepsilon} e^{V(x_o)/\varepsilon} \frac{2}{\pi}\sqrt{|V''(x)|V''(x_o)} \tag{5.25}$$

in agreement with (5.16). On the other hand, the result (5.21) is much more versatile than the eigenfunction calculation. First, ε need not be small, so that (5.21) can be used to describe catalysis reactions (an application would be to the system considered in (6)). Second, we can allow for the experimentally true fact that when the system is prepared, not all the molecules are exactly at x_o. Instead, there is a distribution of molecules,

$$G(x)dx = \Pr\{\tilde{x}(o) \in (x, x+dx)\} \tag{5.26}$$

Then, instead of $1/\bar{t}(x_o)$ we should define the rate constant as

$$\lambda_o = 1/\langle\bar{t}(x)\rangle$$

where

$$\langle\bar{t}(x)\rangle = \int \bar{t}(x)G(x)dx \tag{5.27}$$

is the ensemble average of $\bar{t}(x)$.

The expected time formalism is much more versatile than the Kramers-Miller-Ludwig approach. In figures 2 and 3, we compare the CTST, modified Kramers (eigenvalue) and expected time formulations for the rate constant. The potential used for the calculations was

$$V(x) = -\frac{1}{3}x^3 + \alpha x \tag{5.28}$$

for which $Q = \frac{4}{3}x^{3/2}$

As ε decreases, the Kramers and expected time formulations converge, as is expected from the asymptotic analysis. The CTST provides a reasonable estimate of the rate constant, which is remarkable in light of the assumptions used to derive CTST.

In figure 3, we compare the three theoretical forms of the rate constant with Monte Carlo experiments (500 trials).

THE TRANSMISSION COEFFICIENT

Up to this point, the transmission coefficient κ is unspecified. We now will provide an exact definition of the transmission coefficient and will show how to calculate it. Let $u(x)$ be defined as

$$u(x) = \Pr\{\tilde{x}(t) \text{ crosses } x=x_1 \text{ before } x=x_0 \mid \tilde{x}(o)=x\} \tag{5.29}$$

Then $u(x)$ satisfies a stationary version of (3.8):

$$0 = \varepsilon \frac{\partial^2 u}{\partial x^2} + F(x) \frac{\partial u}{\partial x} \tag{5.30}$$

with boundary conditions

$$u(x_o) = 0 \qquad u(x_1) = 1 \tag{5.31}$$

The transmission coefficient is defined as

$$\kappa = u(\hat{x}) \tag{5.32}$$

Namely, κ is the probability that an activated complex becomes a product before returning to the reactant state.

The solution of (5.30) is

$$u(x) = \frac{\int_{x_o}^{x} e^{V(s)/\varepsilon} ds}{\int_{x_o}^{x_1} e^{V(s)/\varepsilon}\, ds} \tag{5.33}$$

The structure of the potential energy surface around $\hat{x}$ will completely determine the transmission coefficient. If the potential is symmetric about $\hat{x}$ and $|V''(\hat{x})|$ is bounded away from zero, then Laplace's method yields (figure 4a), as expected

$$\kappa \sim \tfrac{1}{2} + o(\varepsilon) \tag{5.34}$$

On the other hand, it is possible that κ is close to zero (figure 4b) or much close to 1 (figure 4c), depending upon the shape of the potential surface (figure 4). However, since detailed knowledge of the potential surface around $\hat{x}$ is only needed, it should be possible to calculate κ for many cases of interest.

The diffusion model thus provides a way to calculate the transmission coefficient, which was previously (in TST) treated as an empirical parameter. In table 1, we compare the theoretical transmission coefficient with Monte Carlo experiments, for the potential (5.28).

LIFETIME OF THE ACTIVATED COMPLEX

Many reactions proceed according to a mechanism in which a true reactant complex is formed, e.g.,

$$F + C_2H_4 \rightarrow C_2H_4F \rightarrow C_2H_3F + H \tag{5.35}$$

In such a case, the potential energy surface will have a double minimum structure as shown in figure 5. The complex is formed in the well at $\hat{x}$. The lifetime is the time that the complex remains in the well. We pick two points a,b with $a < \hat{x}_-$, $b > \hat{x}_+$ (figure 5). The mean lifetime of the complex will satisfy

$$-1 = \varepsilon \frac{\partial^2 \bar{t}}{\partial x^2} + F(x) \frac{\partial \bar{t}}{\partial x} \tag{5.36}$$

$$\bar{t}(a) = \bar{t}(b) = 0 \tag{5.37}$$

In (5.36), $\bar{t}(x)$ is the expected time to hit a or b, given that $\tilde{x}(o) = x$.

The solution of (5.36,37) is

$$\begin{aligned} \bar{t}(x) &= \frac{1}{\varepsilon}\int_a^x e^{V(S)/\varepsilon}\int_a^S e^{-V(y)/\varepsilon}dydS \\ &- \frac{1}{\varepsilon}\left\{\frac{\int_a^x e^{V(S)/\varepsilon}dS}{\int_a^b e^{V(S)/\varepsilon}dS}\right\}\int_a^b e^{V(S)/\varepsilon}\int_a^S e^{-V(y)/\varepsilon}dydS \end{aligned} \tag{5.38}$$

A definition of the lifetime of the activated complex is then

$$\tau_{ac} = \bar{t}(\hat{x}) \tag{5.39}$$

On the other hand, when experiments are performed, activated complexes are produced according to some distribution $H(x)$. Thus, a better definition of the lifetime of the activated complex is

$$\tau_{ac} = E_H(\bar{t}(x)) \tag{5.40}$$

$$= \int_{\hat{x}_-}^{\hat{x}_+} \bar{t}(x)dH(x) \tag{5.41}$$

AN APPLICATION: BIPROTONIC PHOTOTAUTOMERSION

The phenomenon of biprotonic phototautomerism is discussed in (22). A double potential well is present (figure 6)*. In this case, x represents the length of the H - N hydrogen bond (figure 6b) in 7-azaindole or the H - O bond in the formic acid dimer. The UV and green flouresences in figure 6a correspond to 7-azaindole.

The well at x_o corresponds to the 7-azaindole dimer, at x_1 to the tautomer. The excitation of the molecule in the ground state will produce a distribution $\phi(x)dx$ of molecules in the first excited state. We assume that when the excited molecule reaches $x_o(x_1)$, it flouresces with probability $p_o(p_1)$ or decays radiationlessly with probability $1 - p_o(1 - p_1)$.

*Another problem involving a double potential well, which can be treated by these methods is discussed by D. Chandler in J. Chem. Phys. 68:2959(1978).

Let

$$u(x) = \Pr\{\text{molecule reaches } x_o \text{ before } x_1 | \text{starts at } x\} \tag{5.42}$$

then $u(x)$ satisfies the backward equation

$$u = \varepsilon u_{xx} + F(x)ux \tag{5.43}$$

$$u(x_o) = 1 \qquad u(x_1) = 0 \tag{5.44}$$

Assume that the events {reaching $x_o(x_1)$} and {flourescing from $x_o(x_1)$} are independent. Also, we assume that all molecules with $x \le x_o$ ($\ge x_1$) reach $x_o(x_1)$ and flouresce with probability $p_o(p_1)$.

Let

$$I(x) = \frac{p_o u(x)}{p_1(1 - u(x))} \qquad x_o < x < x_1 \tag{5.45}$$

Then $I(x)$ will represent a conditional ratio of UV/green flourescence intensities. The total flourescence intensity is

$$I = \int_{x_o}^{x_1} I(x)\phi(x)dx + \frac{p_o \int_{-\infty}^{x_o} \phi(x)dx}{p_1 \int_{x_1}^{\infty} \phi(x)dx} \tag{5.46}$$

The first term in (5.41) is the contribution to the flourescence of excited molecules initially in $[x_o, x_1]$. The second term is the contribution from molecules with $x \ge x_1$ or $x \le x_o$.

SECTION 6

CALCULATION OF SPECTRA

Very often, we are interested in the shape of the "absorption" spectrum of a bond, $I(\omega)$. Let $\phi(\tau)$ be the correlation function of $\tilde{x}(t)$:

$$\phi(\tau) = E\{\tilde{x}(t + \tau)\tilde{x}(t)\}. \tag{6.1}$$

The correlation function and spectrum are related by

$$I(\omega) = \int e^{-i\omega\tau} \phi(\tau)d\tau \tag{6.2}$$

In this section, we show how the spectrum can be approximately calculated by using the diffusion model. First, consider the conditional correlation function

$$\phi(\tau)_{\bar{x}} = E\{\tilde{x}(t + \tau)\tilde{x}(t) | \tilde{x}(t) = \bar{x}\} \tag{6.3}$$

If $\ell(\bar{x})$ is the density for $\bar{x}$, then

$$\phi(\tau) = \int \phi(\tau)_{\bar{x}} \, \ell(\bar{x})d\bar{x} \tag{6.4}$$

Consequently, we shall calculate $\phi(\tau)_{\bar{x}}$. We use equation (3.9) with initial and boundary conditions

$$p(x, o) = \delta(x - \bar{x})$$

$$\int p(x, t)dx = 1, \quad \lim_{x^2 \to \infty} p(x,t) = 0 \qquad (6.5)$$

Following Ludwing (16), we seek a solution of (6.5) in the form

$$p(x, t) = e^{-\psi(x,t)/\varepsilon} \sum_{k=0}^{\infty} Z_k \varepsilon^k \qquad (6.6)$$

with $\psi(x, t)$ and $Z_k(x, t)$ $k = 0, 1, 2, \ldots$ to be determined. In many cases, it is sufficeint to use only the first term, which will be accurate to order ε:

$$p(x,t) \sim Z_o e^{-\psi(x,t)/\varepsilon} , \qquad (6.7)$$

i.e., Z_o is a "normalization" factor. After derivatives are evaluated and substituted into (3.9), terms are collected according to powers of ε. The leading term is $0(e^{-\psi/\varepsilon}/\varepsilon)$ and vanishes if

$$\psi_t + F(x)\psi_x + \psi_x^2 = 0 \qquad (6.8)$$

Ludwig (16) has shown how this equation can be solved by the method of characteristics. We will not repeat his argument here. We note that (6.8) corresponds to a "Hamiltonian"

$$H = F(x)p + p^2 \qquad (6.9)$$

and to "rays" (where $p=\psi_x$)

$$\frac{dx}{dS} = F(x) + 2p\,, \quad \frac{dp}{dS} = -F_x(x)p \quad \frac{dt}{dS} = 1 \tag{6.10}$$

Along these rays

$$\frac{d\psi}{dS} = p^2 \tag{6.11}$$

The rays cover the phase plane. Hence, by following a sufficient number of rays from $\bar{x}$ for a time τ, it is possible to construct (see figure 7):

$$p_{\bar{x}}(x,\ \tau)dx = \Pr\{\tilde{x}(\tau)\in(x,\ x + dx)\,|\,\tilde{x}(o) = \bar{x}\} \tag{6.12}$$

The conditional correlation function is them

$$\phi_{\bar{x}}(\tau) = \int x p_{\bar{x}}(x,\ \tau)dx \tag{6.13}$$

Finally, the correlation function is

$$\phi(\tau) = \int \ell(\bar{x})\left[\int x p_{\bar{x}}(x,\ \tau)dx\right]d\bar{x} \tag{6.14}$$

and the spectrum is

$$I(\omega) = \int e^{-i\omega\tau}\int \ell(\bar{x})\left[\int x p_{\bar{x}}(x,\ \tau)dx\right]d\bar{x}d\tau \tag{6.15}$$

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APPENDIX A

THE ENERGY METHOD

In this appendix, we briefly describe an alternative formulation of the problem based on the position-energy phase space rather than the position-velocity phase space. A special case of this approach was used by Kramers (1) and Visscher (23). Our approach follows Stratonovich (24). Consider equations (2.17, 2.18). The total energy of the system is

$$E = \tfrac{1}{2}mv^2 + V(x) \tag{A-1}$$

Hence

$$dE = mvdv + V_x dx \tag{A-2}$$

Since $F(x) = -V_x$, (A-2) and (2.17), (2.18) imply that

$$dx = \sqrt{2/m(E - V(x))}\ dt \tag{A-3}$$

$$dE = 2\eta\sqrt{\frac{2}{m}(E-V(x))}\ dt + \sqrt{\frac{4k_BT\eta}{m}(E-V(x))}\ dW \tag{A-4}$$

The Fokker-Planck equation corresponding to (A-3, A-4) is

$$\begin{aligned} p_t(t,x,E) = &-\frac{\partial}{\partial x}\left[\sqrt{\frac{2}{m}(E-V(x))}\,p\right] - 2\eta\frac{\partial}{\partial E}\left[\sqrt{\frac{2}{m}(E-V(x))}\,p\right] \\ &+ \frac{2k_BT\eta}{m}\frac{\partial^2}{\partial E^2}\left[(E-V(x))p\right] \end{aligned} \tag{A-5}$$

In order to obtain the results in (1) and (23), we assume that the conditional density $p(x|E)$ is

$$p(x|E) = \begin{cases} \text{const} \sqrt{E - V(x)} & V(x) < E \\ 0 & \text{otherwise} \end{cases}$$

Then a simple averaging (as in (23), page 117-119) yields an equation for the density $\bar{p}(t, E)$ in E-space only:

$$\bar{p}_t(t, E) = 2\eta \frac{\partial}{\partial E}\left[\frac{\gamma(E)}{\gamma'(E)} \bar{p}\right] + \frac{2k_B T\eta}{m} \frac{\partial^2}{\partial E^2}\left[\frac{\gamma(E)}{\gamma'(E)} \bar{p}\right] \qquad \text{(A-6)}$$

In equation (A-6)

$$\gamma(E) = \tfrac{1}{2}\sqrt{\frac{2}{m}} \int_{R(E)} \sqrt{E - V(x)}\, dx$$

$$\gamma'(E) = \tfrac{1}{2}\sqrt{\frac{2}{m}} \int_{R(E)} (E - V(x))^{-\frac{1}{2}} dx \qquad \text{(A-7)}$$

where $R(E) = \{x: V(x) < E\}$. Equation (A-6) is the equation of diffusion in energy space used in (1) and (23).

APPENDIX B

MULTIPLE BARRIERS

In the body of the paper, we did not consider the possibility that more than one energy barrier must be crossed. The results, however, generalize immediately. For example, we consider the expected time result (5.23), where $V(x)$ now has k maxima $\hat{x}_{oj}$ $j = 1, \ldots, k$ and minima x_{oj}, $j = 1, \ldots, k$. Then the asymptotic evaluation of (5.23) is

$$t(x_o) \sim \frac{1}{\varepsilon} \sum_{j}^{k} \left(\frac{\pi\varepsilon}{2|V''(\hat{x}_j)|} \right)^{\frac{1}{2}} \left(\frac{\pi\varepsilon}{2V''(x_{oj})} \right)^{\frac{1}{2}} e^{V(\hat{x}_j)/\varepsilon} e^{-V(x_{oj})/\varepsilon} \qquad \text{(B-1)}$$

where $x_o \equiv x_{o1}$. The other asymptotic results are also replaced by expressions involving sums over various contributions.

CAPTIONS

Figure 1: Typical potentials of interest in this paper: a) a Lennard-Jones like potential; b) a double-minimum potential (e.g., hydrogen bonded tautomers).

Figure 2: A comparison of numerical results using CTST, the eigenvalue formulation and the expected time formulation for the reaction rate constant.

Figure 3: Comparison of CTST, the eigenvalue formulation and expected time formulations for the reaction rate constant with Monte Carlo experiments.

Figure 4: Transmission coefficient in the ES formulation. A steeped barrier, for which $\kappa=\frac{1}{2} + 0(\varepsilon)$; b) a flat barrier, for which κ is close to 0; c) an almost discontinuous barrier, for which κ is close to 1.

Figure 5: Potential energy surface for a reaction proceeding by complex formulation.

Figure 6: Potential energy surface for biprotonic phototautomerism.

Figure 7: A schematic illustration of how the ray method can be used to numerically construct correlation functions. Rays emanate from the point $\bar{x}$. The intersection of the line $t = \tau$ and the rays determine those points that can be reached from $\bar{x}$ in time. The density on these points is $p_{\bar{x}}(x, \tau)$ and is calculated along the rays.

Table 1: A comparison of the theoretical transmission coefficient with Monte Carlo experiments.

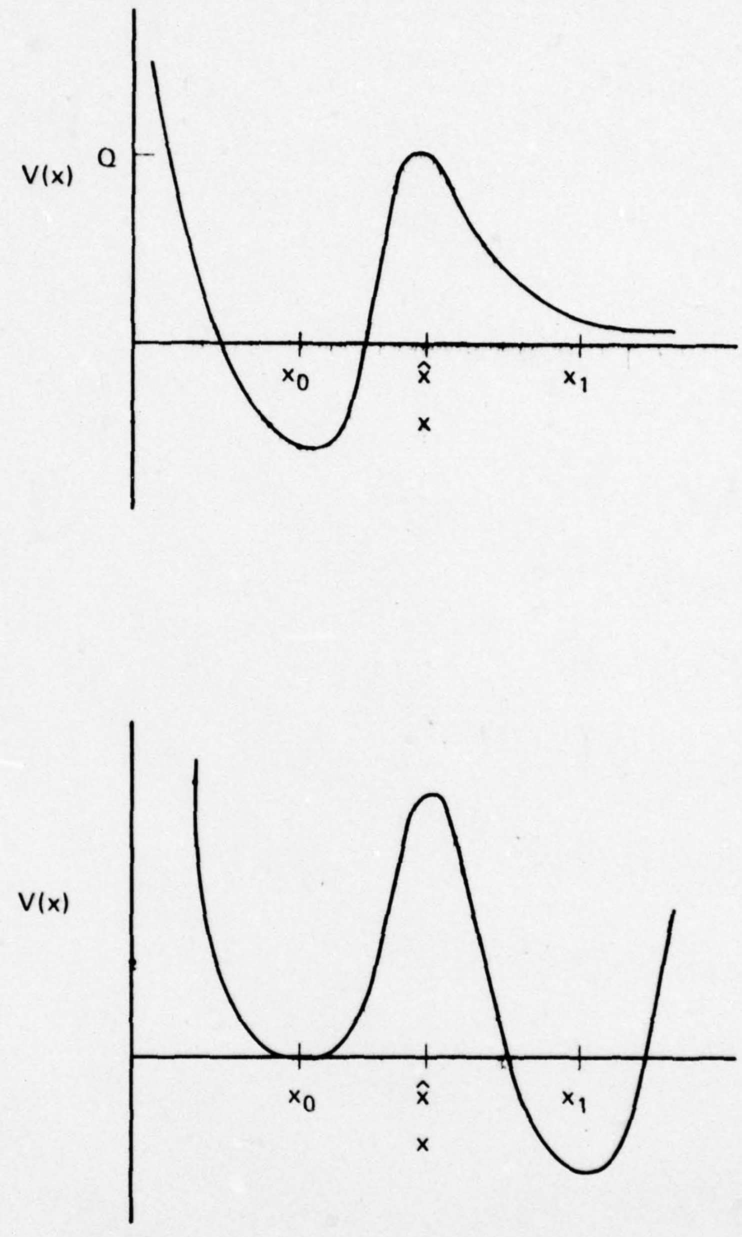
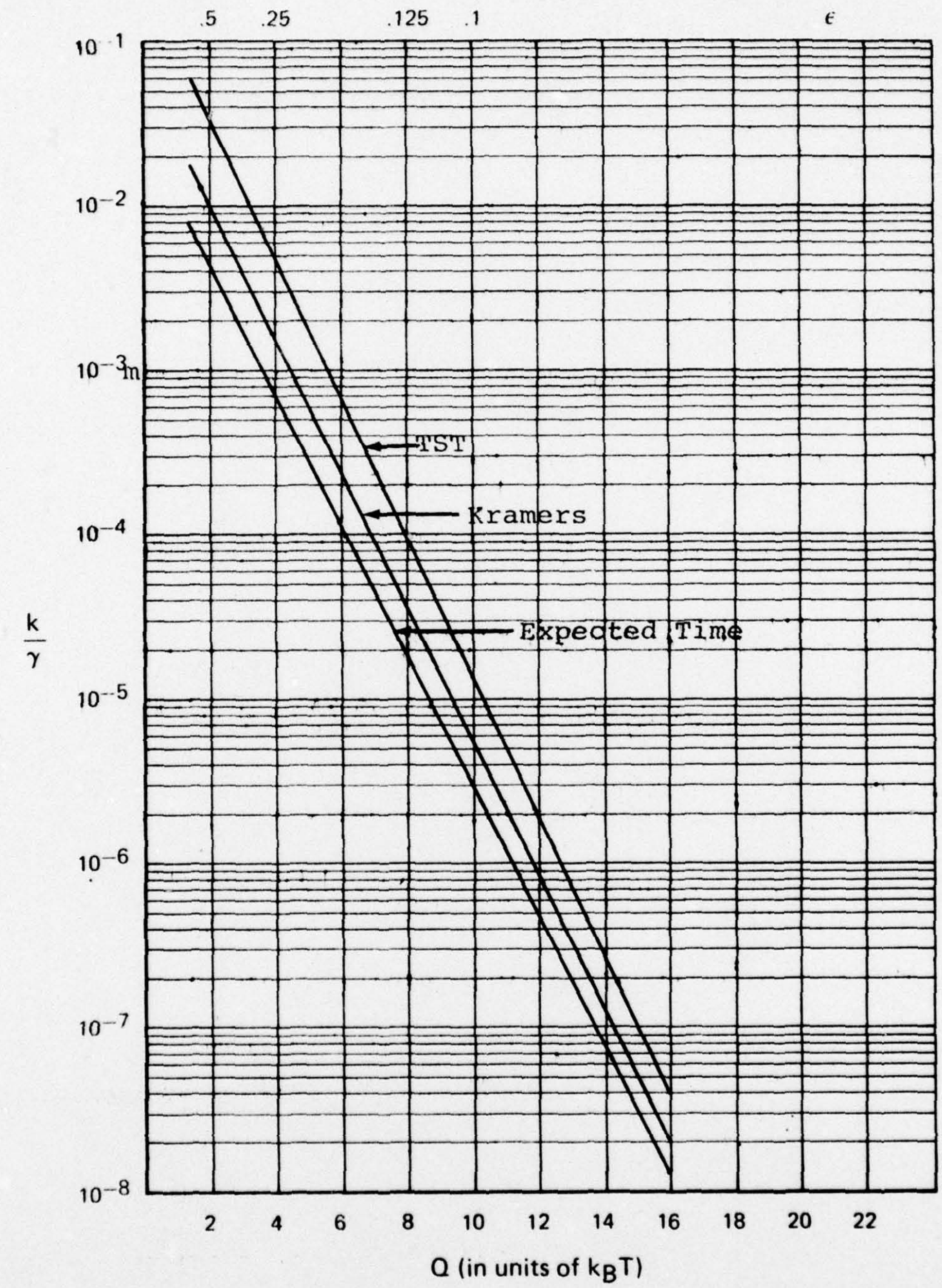


FIGURE 1



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TST
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6
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10
12
14
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18
20
22
Q (in units of k_BT)

FIGURE 2

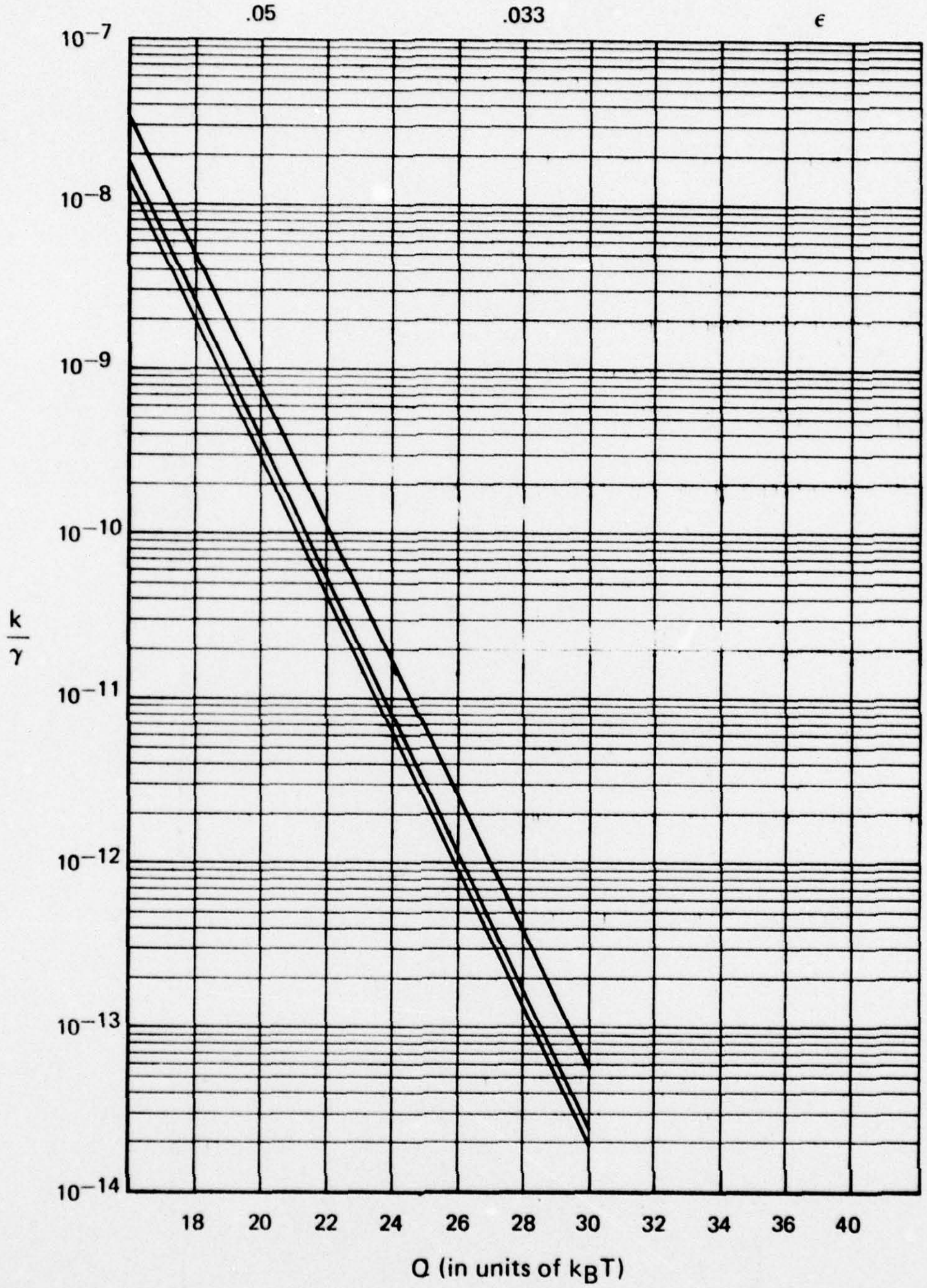
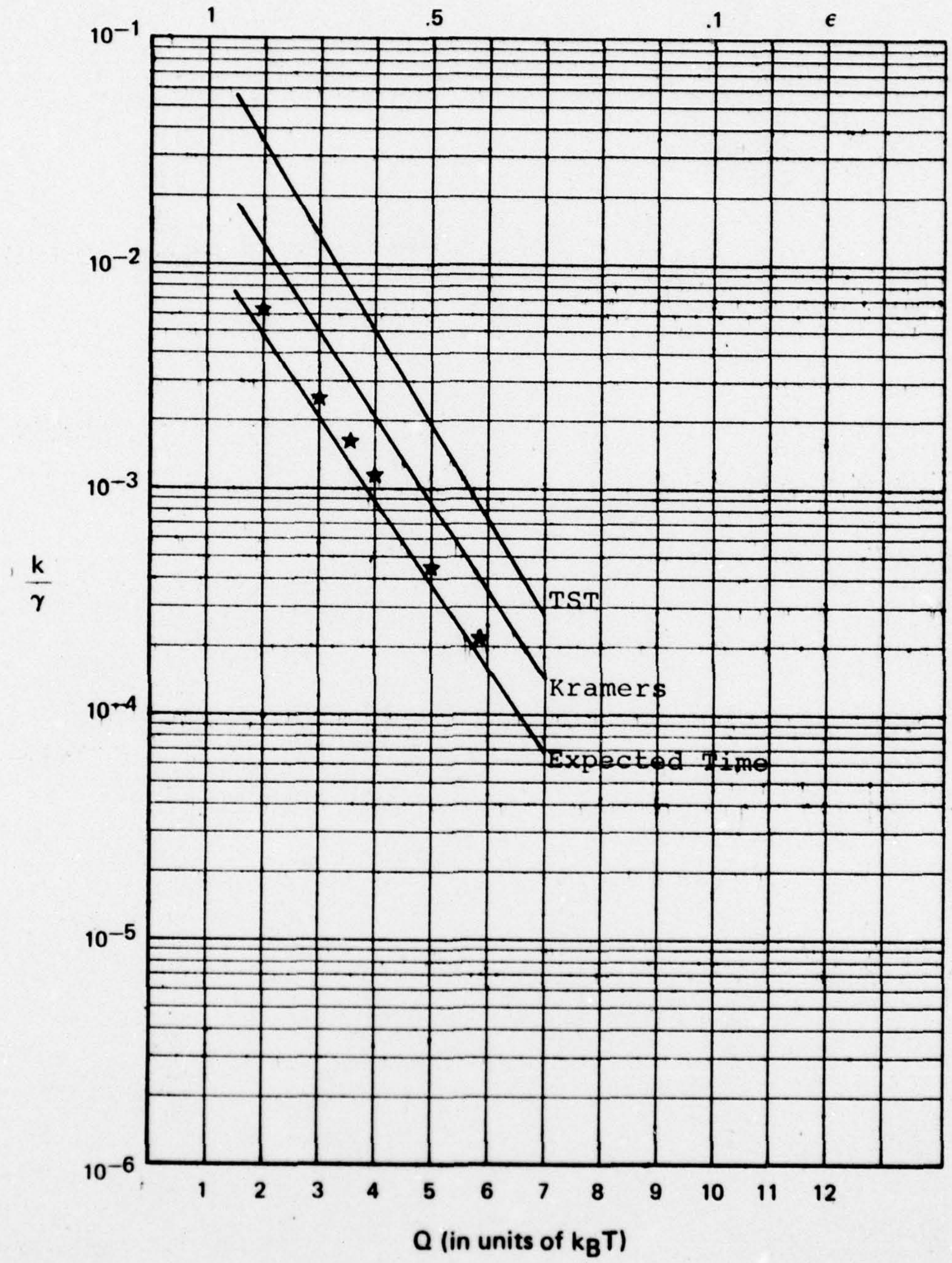


FIGURE 2 Continued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$\frac{k}{\gamma}$
TST
Kramers
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11
12
Q (in units of k_BT)

FIGURE 3

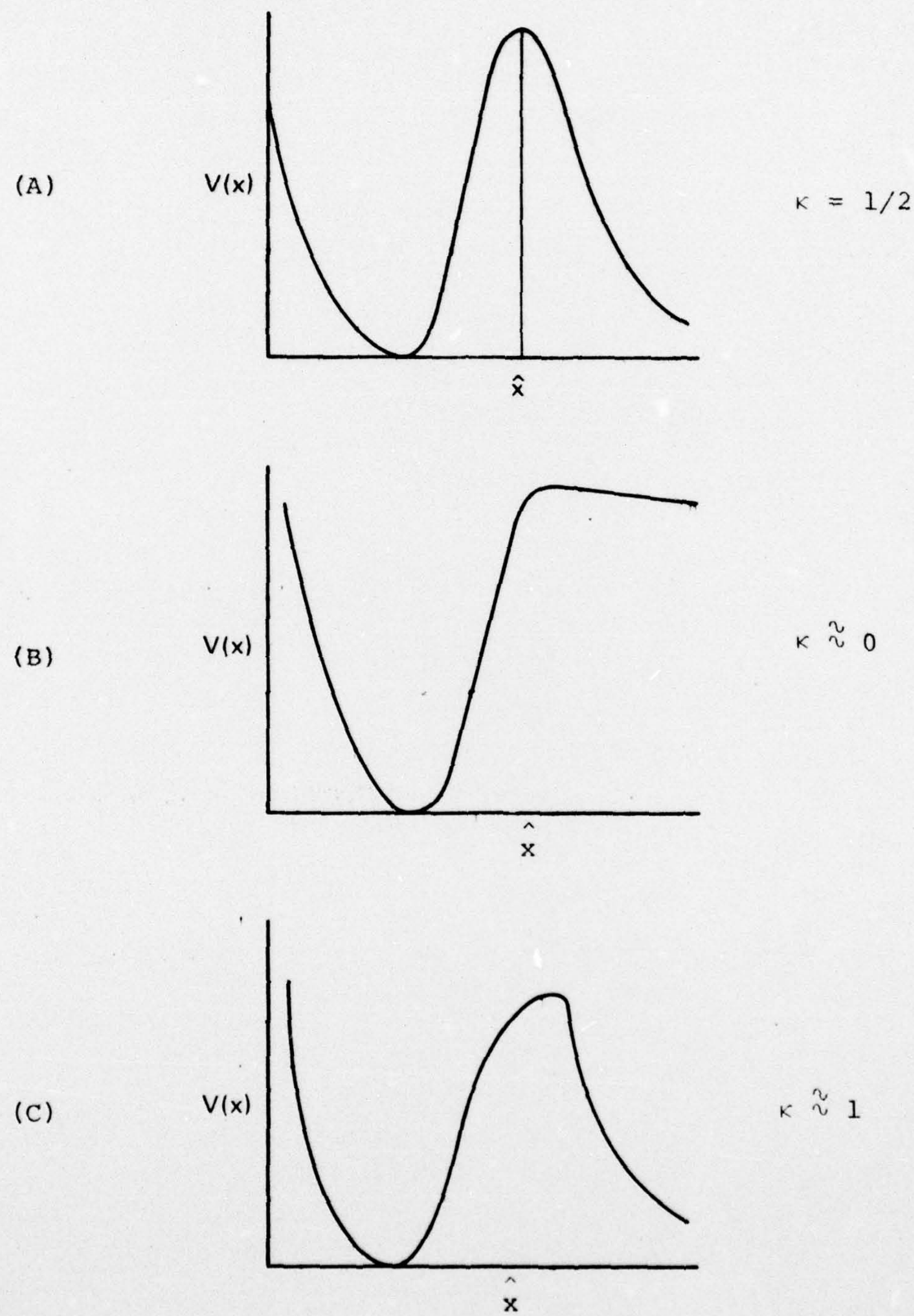


FIGURE 4

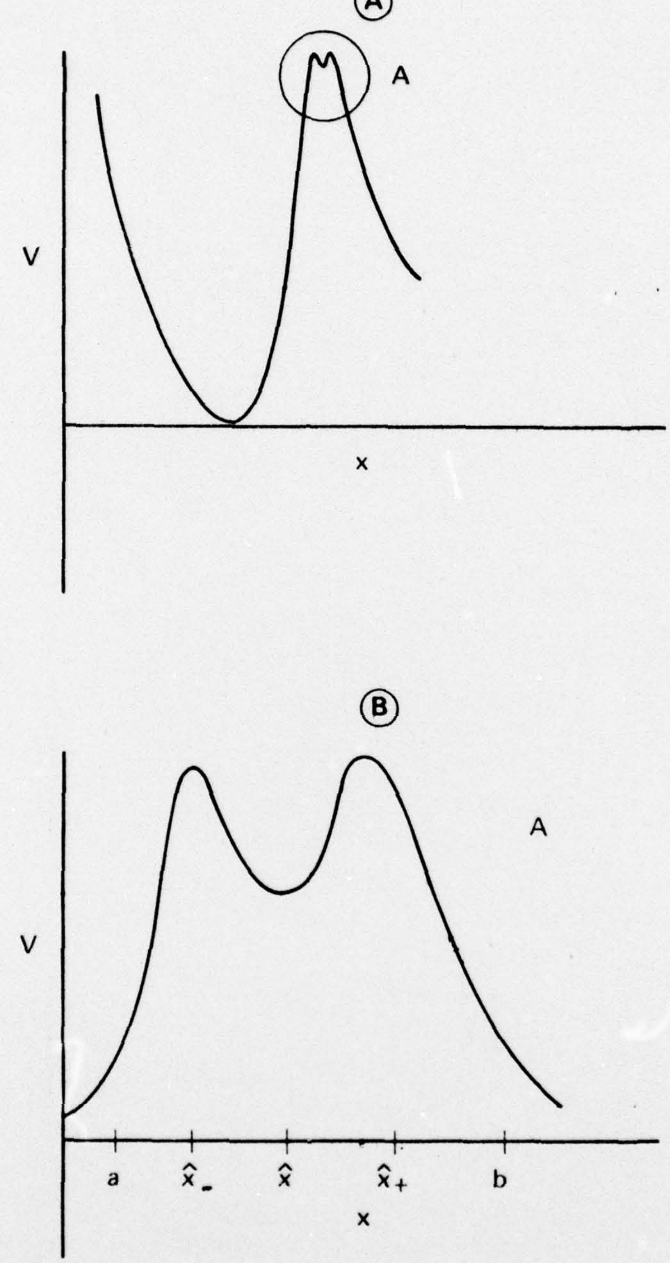
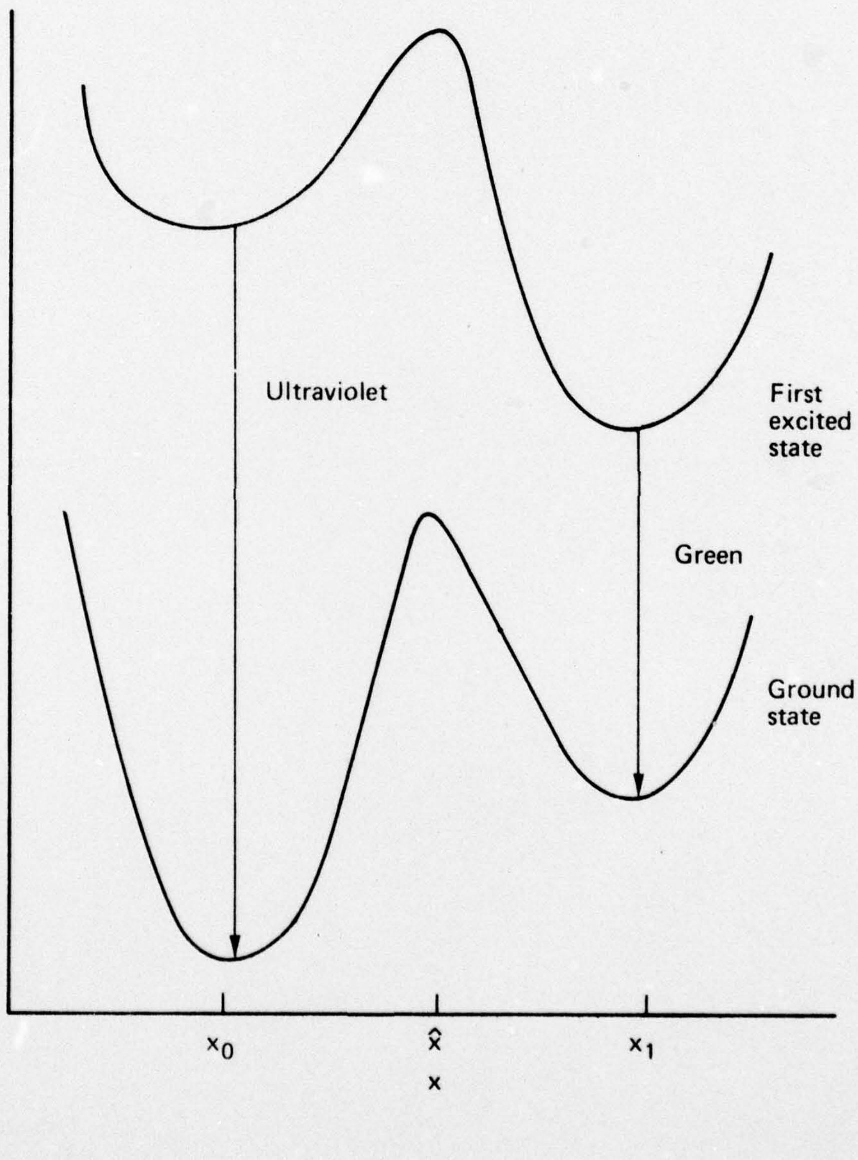
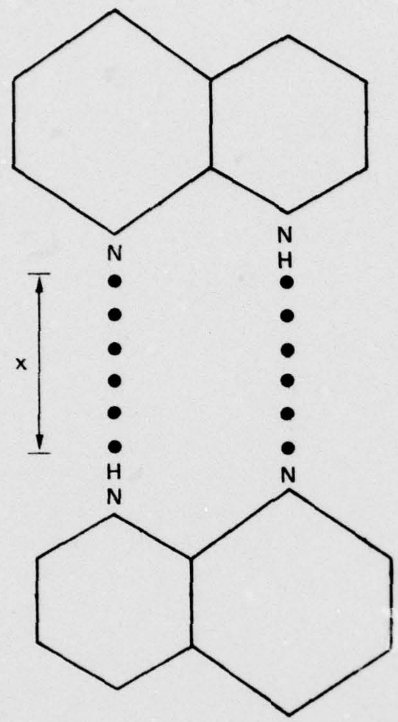


FIGURE 5



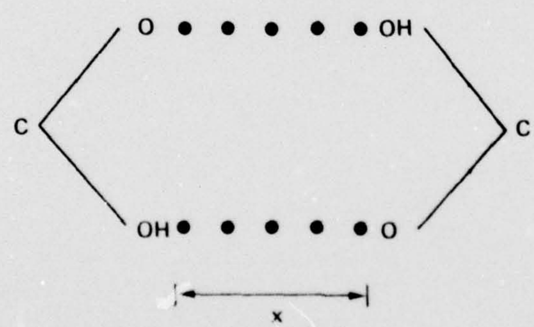
Ultraviolet
First
excited
state
Green
Ground
state
x_0
$\hat{x}$
x_1
x

FIGURE 6



b.

7 azaindol dimer



c.

Formic acid dimer

FIGURE 6 Continued

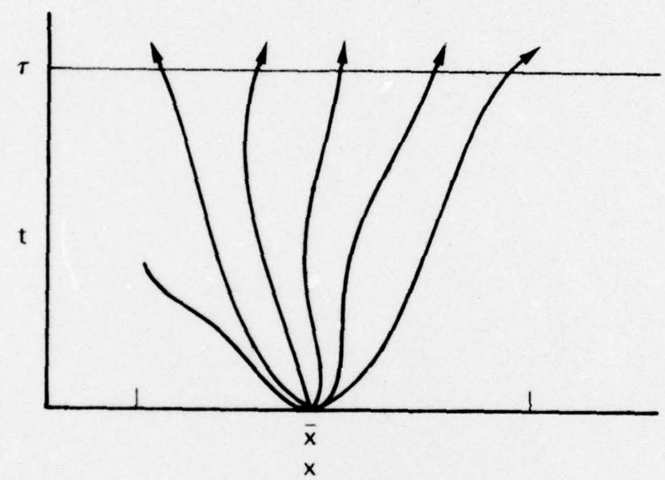


FIGURE 7

TABLE 1

A COMPARISON OF THE THEORETICAL TRANSMISSION COEFFICIENT WITH MONTE CARLO EXPERIMENTS.

Q(in units of k_BT)	$\hat{x}$	κ(Theory)	κ(MC)*
3	1.31	.58	.58
13	2.14	.53	.53
23	2.58	.52	.52

*2500 Monte Carlo simulations were performed.

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