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Diffusion theory of reaction rates for multiple potential barriers

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According to the diffusion theory of reaction rates (proposed by H. Kramers in 1940[1]) as molecules move in physical space, they execute a random walk in a field of force in reaction coordinate space. The original paper of Kramers spawned many others (see, e.g., Refs. 2–14). In these papers, the diffusion process occurs in a field of force in which the potential barrier has a single peak separating reactant and product states. There are applications of present interest, however, in which the reactant proceeds to the product by means of many intermediate states, so that there are many potential barriers to overcome. Some examples are weak ionic conductivity in periodic lattices,[14–16] the migration of ligands in biomolecules,[17–20] the photocyle of bacteriorhodopsin;[21–23] and membrane transport.[24–26] In these cases, the method proposed by Kramers for the calculation of the rate constant is difficult to apply, and breaks down if the barrier heights are not large enough. Instead of using the method of Kramers, we shall use the method developed in Ref. 2 (for one-dimensional reaction coordinate potentials) in which the rate constant is calculated exactly and the results of Kramers are obtained as a certain limit (that of high barriers).

When reaction rates in solution are studied experimentally, two parameters that can be adjusted are the temperature and viscosity of the solution. Consequently, the dependence of reaction rate on temperature and viscosity will be studied in this paper so that the theory can be used when analyzing rate data. In the classic setting for analyzing rate data, the rate constant is given by $k = A e^{-Q/k_B T}$, where k is the rate constant, Q the barrier height, k_B is Boltzmann's constant, and T is temperature. Thus, a plot of $\log k$ against $1/k_B T$ has slope $-Q$ and intercept $\log A$. In this paper, we show that the simple interpretation changes for potentials with many barriers.

In the Einstein–Smoluchowski limit of the diffusion theory,[2] the reaction coordinate $X(t)$ is assumed to satisfy the stochastic differential equation

$$dX = \frac{F(X)}{\eta} dt + \sqrt{\frac{2k_B T}{\eta}} \, dW \ . \tag{2.1}$$

In this equation, η is proportional to the viscosity, k_B is Boltzmann's constant, T is absolute temperature, and $W(t)$ is Brownian motion.[27] The force $F(x)$ is derived from the potential $V(x)$, so that $F(x) = -V'(x)$. The potential is assumed to have a local minimum at $x_R = 0$, corresponding to the reactant state, and at x_P corresponding to the product state, and n interior barriers. Thus, there are $2n - 1$ interior stationary points x_j, labeled so that local maxima have odd indices and local minima have even indices. The potential is assumed to increase monotonically for $x < x_R$ and $x > x_P$.

If $\hat{T}(x)$ is the mean time to reach the x_P state, starting at the value $X(0) = x$, then according to the diffusion theory of reactions $\hat{T}(x)$ is exactly given by[2]

$$\hat{T}(x) = \frac{\eta}{\beta} \int_x^{x_P} \exp[V(s)/\beta] \int_{-\infty}^s \exp[-V(y)/\beta] \, dy \, ds, \tag{2.2}$$

here $\beta \equiv k_B T$.

Equation (2.2) is exact. The rate constant is defined as the reciprocal of the average of $\hat{T}(x)$ against the initial density for $X(0)$. Regardless of the form of this distribution or the number of barriers, from Eq. (2.2) we see that the rate constant is proportional to η^{-1}.

Thus we conclude that a simple extension of the Kramers model to the case of n barriers does not explain recent experiments[20,23] in which the rate constant was found to have a $\eta^{-\kappa}$ dependence, with $0 < \kappa < 1$. Equation (2.2) holds for barriers of arbitrary height. The formula that Kramers derived[1] is valid for barriers that are large so that we now study the large barrier limit of $\hat{T}(x_R)$.

To do this, let Q_j be the height of the jth barrier and let Q be the minimum value of Q_j, $j = 1, \ldots, n$.

In the large barrier approximation, we assume that

$Q \gg \beta$. Define $\hat{V} = V/Q$ and $\epsilon = \beta/Q$, so that Eq. (2.2) becomes

$$\hat{T}(x_R) = \frac{\eta}{\beta} \int_{x_R}^{z_3} \exp[\hat{V}(s)/\epsilon] \int_{-\infty}^{s} \exp[-\hat{V}(y)/\epsilon] dy ds . \quad (2.3)$$

Let z_j be the solutions of $\hat{V}(z) = Q/2$; if there are n barriers then there are $2n + 2$ solutions of this equation. We order the solutions so that $z_1 < x_R$ and $z_{2n+2} > x_P$. Rewrite equation (2.3) as

$$\hat{T}(x_R) = \frac{\eta}{\beta} \left\{ \int_{x_P}^{z_3} \exp[\hat{V}(s)/\epsilon] \int_{-\infty}^{s} \exp[-\hat{V}(y)/\epsilon] dy \, ds \right.$$

$$+ \sum_{j=3, \text{ odd}}^{2n-3} \int_{z_j}^{z_{j+2}} \exp[\hat{V}(s)/\epsilon] \int_{-\infty}^{s} \exp[-\hat{V}(y)/\epsilon] dy \, ds$$

$$\left. + \int_{z_{2n-1}}^{x_P} \exp[\hat{V}(s)/\epsilon] \int_{-\infty}^{s} \exp[-\hat{V}(y)/\epsilon] dy \, ds \right\} \quad (2.4)$$

When the barriers are high, so that ϵ is small, each integral in Eq. (2.4) can be analyzed by Laplace's method.[28] When this is done, one obtains (returning to physical variables)

$$\hat{T}(x_R) \sim 2\pi\eta \sum_{j \text{ even}} \frac{\exp\{[V(x_{j+1}) - V(x_j)]/\beta\}}{[V''(x_j) |V''(x_{j+1})|]^{1/2}} . \quad (2.5a)$$

In this equation, we interpret $x_0 = x_R$. The time given by Eq. (2.5a) is a sum of times to cross the separate barriers on the way to x_P from x_R. From now on, all summations are taken over j even.

If $X(0)$ is initially concentrated at x_R, the observed rate constant is

$$k \sim \frac{1}{2\pi\eta} \left(\sum \frac{\exp\{[V(x_{j+1}) - V(x_j)]/\beta\}}{[V''(x_j) |V''(x_{j+1})|]^{1/2}} \right)^{-1} . \quad (2.5b)$$

Let us now consider how the formula (2.5b) could be used in the analysis of rate data. First consider the case of n barriers of equal height, but differing curvatures. Then Eq. (2.5b) becomes

$$k \sim \frac{1}{2\pi\eta} e^{-Q/\beta} \left\{ \sum [V''(x_j) |V''(x_{j+1})|]^{-1/2} \right\}^{-1} . \quad (2.6)$$

From Eq. (2.6) we see that a plot of $\log(k)$ against $1/\beta$ has slope $-Q$ and intercept determined by the viscosity and the frequency factors, but one can not determine the number of barriers from such a plot.

To consider unequal barriers, let $Q_j = V(x_{j+1}) - V(x_j)$, $\gamma = 1/\beta$, and let $f_j = [V''(x_j) |V''(x_{j+1})|]^{-1/2}$ so that

$$k \sim \frac{1}{2\pi\eta} \left(\sum e^{\gamma Q_j} f_j \right)^{-1} , \quad (2.7)$$

then

$$\log k \sim -\log(2\pi\eta) - \log\left(\sum e^{\gamma Q_j} f_j \right) \quad (2.8)$$

so that

$$\frac{\partial}{\partial \gamma} \log k \sim \frac{-1}{\sum e^{\gamma Q_j} f_j} \sum Q_j f_j e^{\gamma Q_j} . \quad (2.9)$$

Equation (2.9) indicates that a plot of $\log k$ against $1/k_B T$ does not provide a simple interpretation of the barrier heights.

In the special case of constant curvature, but differing barriers, Eq. (2.9) becomes

$$\frac{\partial}{\partial \gamma} \log k \sim \frac{\sum Q_j e^{\gamma Q_j}}{\sum e^{\gamma Q_j}} . \quad (2.10)$$

Equation (2.10) could indicate the presence of n barriers, but the slopes of the plot of $\log k$ versus $1/k_B T$ will not give accurate values for the barriers.

We conclude by considering the temperature dependence of the rate formula (2.3) near a critical point of the potential. A critical point, or phase transition point, now refers to a point in parameter space where the first, second, and third derivatives of the potential vanish. In many physical cases, the parameter is the temperature. Near the critical temperature, the asymptotic result (2.5) is no longer valid. Instead, a different expansion is needed.

In order to obtain this expansion, proceed as follows. For notational convenience, index $V(y)$ by $V(y; \alpha)$, where it is understood that when $\alpha = \alpha_c$, a critical value, $V'(x_j, \alpha_c) = V''(x_j, \alpha_c) = V'''(x_j, \alpha_c) = 0$. When α is near α_c, when finding the asymptotic expansion of Eq. (3.4), one needs the expansion

$$\hat{V}(z) = \hat{V}(x_j) + \hat{V}'(x_j)(z - x_j)$$

$$+ \hat{V}'' \frac{(z - x_j)^2}{2} + \hat{V}''' \frac{(z - x_j)^3}{3!} + \hat{V}^{iv} \frac{(z - x_j)^2}{4!} ,$$

instead of a three-term Taylor expansion. At the critical value α_c, the expansion (2.5) is replaced by (also see Ref. 29)

$$\hat{T}(x_R) \sim \frac{\eta}{\sqrt{\beta}} c_4^2 \sum_j \frac{\exp[\hat{V}(x_j) + \hat{V}(x_{j+1})]/\beta}{[\hat{V}^{iv}(x_j) |\hat{V}^{iv}(x_{j+1})|]^{1/4}} \quad (2.11)$$

In this equation

$$c_4 = \int_{-\infty}^{\infty} \exp(-s^4/4) ds . \quad (2.12)$$

Equation (2.1) indicates that near a critical point

$$\log k \sim \frac{1}{2} \log \beta - \log\left\{ \sum \frac{\exp(Q_j/\beta)}{[\hat{V}^{iv}(x_j) |\hat{V}^{iv}(x_{j+1})|]^{1/4}} \right\} + \text{constant} , \quad (2.13)$$

so that there will be a term in $\log k$ directly proportional to the log of inverse temperature.

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Slater transition state calculations of valence electron spin–orbit splitting in atoms

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The multiplet structure of lighter atoms within the local density functional scheme[1] has been calculated earlier[2,3] as the difference between the total electronic energy corresponding to the initial and final state, respectively (ΔSCF method[4]). In a recent paper Schwartz[5] has shown that the potential due to Hedin and Lundquist[6] (HL) coupled with the Slater transition state (TS) method[7] provides reliable values of the first ionization potential in free atoms. In this communication we report the results of the TS calculation of the valence electron binding energy corresponding to the $np_{1/2}$ and $np_{3/2}$ electrons in Ar($n = 3$), Kr($n = 4$), Xe($n = 5$), Ba($n = 5$), and the $nd_{3/2}$ and $nd_{5/2}$ electrons in Hg($n = 5$) and Pb($n = 5$), respectively. In the TS method the ionization potential of a shell (n_j) is equated to the eigenvalue of the shell with half an electron removed. We have used the relativistic Hartree–Fock–Slater computer program[8-10] modified to include the HL potential according to the definition $V_{HL}(r) = \beta(r_s) V_{XS}(r)$, where

$$\beta(r_s) = (2/3)[1 + 0.0316 r_s \ln(1 + 24.3/r_s)] ,$$

with $r_s = [4\pi\rho(r)/3]^{-1/3}$ and $V_{XS}(r_s)$ represents the original Slater exchange potential.

In Table I we have listed the calculated binding energies in eV along with the corresponding experimental results obtained in the gas phase. The theoretical results are found to be in excellent agreement with experiments. For Bi the $6p_{3/2}$ level is predicted as lying above the $6p_{1/2}$ level by 2.3 eV. In conclusion, the present calculations establish the TS method as a reliable alternative to the conventional ΔSCF method for theoretically estimating the valence electron spin–orbit splittings. It would be worthwhile to carry out a similar analysis corresponding to the core electrons.

TABLE I. Comparison of the transition state calculations based on the relativistic Hedin–Lundquist local density potential with the experimental values obtained in the gas phase.[a] All values are given in eV.

Atom	Tr. state	Calc.	Exp.
Ar	$3p_{1/2}^{1.5}$	16.18	15.94
	$3p_{3/2}^{3.5}$	15.97	15.76
Kr	$4p_{1/2}^{1.5}$	14.84	14.65
	$4p_{3/2}^{3.5}$	14.10	14.00
Xe	$5p_{1/2}^{1.5}$	13.59	13.43
	$5p_{3/2}^{3.5}$	12.27	12.13
Ba	$5p_{1/2}^{1.5}$	24.86	24.30
	$5p_{3/2}^{3.5}$	22.59	22.14
Hg	$5d_{3/2}^{3.5}$	16.83	16.70
	$5d_{5/2}^{5.5}$	14.86	14.90
Pb	$5d_{3/2}^{3.5}$	27.76	28.25
	$5d_{5/2}^{5.5}$	25.03	25.28

[a]Experimental values are taken from the compilation by K. D. Sevier, At. Data Nucl. Data Tables 24, 323 (1979).

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