

VARIATIONAL THEORY OF REACTION RATES

JAMES C. KECK,* *Massachusetts Institute of Technology,
Cambridge, Mass., U.S.A.*

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I. INTRODUCTION

The variational theory of reaction rates provides a systematic method for making and improving estimates of reaction rates for systems that can be described classically. It is based on an approach originally used by Marcelin¹ in 1915 and later developed in detail by Wigner,² Horiuti,³ and the writer.⁴ The basic assumption

* Ford Professor of Mechanical Engineering.

of the theory is that a reacting system can be described by the motion of a representative point in the phase space of the system. This phase space is then divided by a trial surface into regions corresponding approximately to the reactants and the products, and the rate at which representative points flow through the surface in one direction is calculated. Clearly, such a calculation gives an upper limit to the true reaction rate since passage at least once through the trial surface is a necessary condition for reaction. Finally, the trial surface is varied to obtain the minimum flow rate, which is the best approximation to the true reaction rate for the given range of variations.

In principle, this procedure can lead ultimately to the true reaction rate since it can be seen from the flow analogy that there exists a set of surfaces that are crossed once and only once by all trajectories leading from reactants to products. In practice, even for three-body reactions, the surfaces corresponding to the true rate are, in general, much too complicated to be dealt with analytically, and we must hope that reasonable approximations can be found. In this connection it should be noted that there is at least one important special case in which the trial surfaces may be relatively simple. This occurs when the collisions between particles are impulsive, so that recrossing of the surfaces becomes negligible. Under these conditions the variational theory gives results in agreement with those obtained from the impulse approximation.

The variational theory is very general in its applications and includes as special cases many of the more familiar classical and semiclassical theories of reaction rates. We shall, therefore, review the basic assumptions on which the theory is based.

The first of these assumptions is that the reactions can be described by using classical mechanics. Although the conditions for this cannot be stated precisely, a rough general criterion is that the reduced wavelength λ of the interacting particles should be small compared with the characteristic length in which appreciable changes in the potential occur. For atomic and molecular interactions, this may be taken as the Bohr radius a_0 , and we obtain the condition:

$$\lambda/a_0 = (I_H m_e / E_k M)^{1/2} < 1, \quad (1.1)$$

where I_H is the ionization potential of hydrogen, m_e is the electron mass, and E_k and M are the kinetic energy and mass of a typical particle. This inequality indicates that, for all particles heavier than hydrogen, classical mechanics should be a reasonable approximation for energies above 10^{-2} eV or temperatures above 100°K . It is pointless to argue about how much less than unity λ/a_0 should be because the division between classical and quantum mechanics is not precise, and in practice it is usually found that, where appreciable averaging of the results is involved, classical mechanics are valid well into the quantum-mechanical domain.

The second assumption is that the interactions between particles can be described by a potential which is a unique function of the relative position coordinates. For atomic and molecular interactions this requires that the Born–Oppenheimer separation shall be valid, so that electronic transitions are forbidden. Although it is now recognized that there are many important exceptions to this rule, it is still expected to hold for a large class of chemical reactions.

The final assumption is that the reacting systems are independent of each other, so that ensemble averages may be taken. For reactions occurring in bulk media, this requires that the systems are sufficiently dilute for the effective range of the interactions to be small compared with the interparticle spacing. An equivalent statement is that the mean free path λ_p of a particle must be large compared with the range of the interaction. This leads to the condition

$$a_0^3 N \sim a_0/\lambda_p \ll 1, \quad (1.2)$$

where N is the particle number density. This is true for most gases away from the critical point.

On the basis of these assumptions, we may now proceed with the formal mathematical development of the variational theory. This is given in Section II. In Section III we use the results of Section II to derive some of the more familiar theories of reaction rates. In Section IV we consider the applications of the theory to the problem of three-body recombination and dissociation, and in the final Section we discuss briefly corrections and extensions of the theory.

II. BASIC EQUATIONS

Consider an ensemble of systems each containing n classical particles interacting with a known potential. The state of each system can be represented by a point in a $3n$ -dimensional phase space, the axes of which are the conjugate momentum and position coordinates (\mathbf{p}, \mathbf{q}) of the particles. Let $\rho(\mathbf{p}, \mathbf{q})$ be the density of such representative points. Then, since the number of points is conserved, ρ satisfies the equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \mathbf{v} = 0, \quad (2.1)$$

where \mathbf{v} is the generalized velocity of a point in phase space and ∇ is the generalized divergence operator. If the Hamiltonian of the systems is $H(\mathbf{p}, \mathbf{q})$, the components of \mathbf{v} may be obtained from the equations

$$\dot{q}_i = \partial H / \partial p_i, \quad \dot{p}_i = -\partial H / \partial q_i. \quad (2.2)$$

These equations determine the flow pattern of points in phase space which move as though they were entrained in an incompressible fluid. This analogy is extremely useful and permits one to describe a chemical reaction as the convection of representative points from one region of phase space to another by the incompressible phase fluid.

We now consider a volume $\Omega(i)$ in phase space corresponding to a particular chemical state i of our system. Integrating (2.1) over this volume we obtain

$$\partial N(i) / \partial t = - \int_{\Omega(i)} (\nabla \cdot \rho \mathbf{v}) \prod_1^{3n} dp_j dq_j, \quad (2.3)$$

where

$$N(i) = \int_{\Omega(i)} \rho \prod_1^{3n} dp_j dq_j \quad (2.4)$$

is the number of systems in the state i . The right-hand side of eqn. (2.3) may now be converted into a surface integral, so that

$$\partial N(i) / \partial t = - \int_{S(i)} \rho (\mathbf{v} \cdot \mathbf{n}) ds, \quad (2.5)$$

where \mathbf{n} is the unit outward normal to ds and $S(i)$ is the surface

bounding $\Omega(i)$. Equation (2.5) merely states that the rate of change of systems in $\Omega(i)$ is equal to the negative of the rate at which they flow out across its boundary.

A. The Reaction Rate

We may now further decompose the surface integral in (2.5) into terms representing the population and depopulation of the state i by reactions leading to and from various final states f . When this is done, eqn. (2.5) becomes

$$\partial N(i)/\partial t = \prod_f [R(i,f) - R(f,i)], \quad (2.6)$$

where

$$R(f,i) = \int_{S(f,i)} \rho(\mathbf{v} \cdot \mathbf{n}) ds \quad (2.7)$$

and $S(f,i)$ is that part of the boundary between i and f on which $(\mathbf{v} \cdot \mathbf{n}) > 0$. Note that $R(f,i)$ is the total rate at which representative points cross the boundary between i and f in one direction. Clearly $R(f,i)$ gives an upper limit to the net reaction rate since all systems which react must cross $S(f,i)$ at least once. It is also clear from the flow analogy that there exists a set of surfaces which are crossed once and only once by trajectories leading from i to f . However, to find these surfaces, one would, in general, have to solve the equations of motion (2.2), and this cannot usually be done. We therefore propose instead to carry out the integration of (2.7) over various trial surfaces and to select the smallest crossing rate as the best approximation to the true reaction rate. This procedure may be carried out either by trial and error or by selecting surfaces depending on a set of parameters which may be varied to yield a minimum rate.

We now wish to obtain an explicit expression for $R(f,i)$ in terms of the canonical coordinates (\mathbf{p}, \mathbf{q}) . Let the partial surface $S(f,i)$, corresponding to reactions leading from i to f , be defined by the set of constraints

$$S(\mathbf{p}, \mathbf{q}) = 0, \quad C(\mathbf{p}, \mathbf{q}) < 0, \quad (\mathbf{v} \cdot \mathbf{n}) > 0, \quad (2.8)$$

which determine respectively the boundary of $\Omega(i)$, the boundary of the final channel, and the direction of flow. The normal to $S(f,i)$ can then be expressed

$$\mathbf{n} = (\nabla S / |\nabla S|)_{S=0}, \quad (2.9)$$

and substitution of this into expression (2.7) gives

$$R(f, i) = \int_{S(f, i)} \rho(\mathbf{v} \cdot \nabla S) |\nabla S|^{-1} ds. \quad (2.10)$$

To obtain the Wigner form of the reaction rate, we substitute

$$\mathbf{v} \cdot \nabla S = dS/dt \quad (2.11)$$

into (2.10), then integrate and differentiate with respect to dS . This yields

$$R(f, i) = \left(\frac{d}{dx} \int_{S(f, i)}^x \int_{S(f, i)} \rho \left(\frac{dS}{dt} \right) \frac{ds dS}{|\nabla S|} \right)_{x=0}. \quad (2.12)$$

Since $|\nabla S|^{-1} dS ds$ is just the differential element of length perpendicular to ds , the factor

$$|\nabla S|^{-1} dS ds = \prod_1^{3n} dp_j dq_j, \quad (2.13)$$

in (2.12) is the volume element in phase space and (2.12) can be written:

$$R(f, i) = \left(\frac{d}{dx} \int_{\Omega(x)} \rho \left(\frac{dS}{dt} \right) \prod_1^{3n} dp_j dq_j \right)_{x=0}, \quad (2.14)$$

where volume of integration $\Omega(x)$ is defined by $S < x$, $C < 0$, and $dS/dt > 0$.

An alternative form of the result may also be obtained from (2.10) by using the equation

$$\mathbf{v} \cdot \nabla S = \prod_1^{3n} J_j, \quad (2.15)$$

where

$$J_j = \left(\frac{\partial H}{\partial p_j} \cdot \frac{\partial S}{\partial q_j} - \frac{\partial H}{\partial q_j} \cdot \frac{\partial S}{\partial p_j} \right) = \frac{dH dS}{dp_j dq_j} \quad (2.16)$$

is the Jacobian of the transformation from (H, S) to (p_j, q_j) . Substituting (2.15) in (2.10) and using (2.13), we find

$$R(f, i) = \int_{S(f, i)} \rho \left(\sum_1^{3n} J_j / |J_1| \right) dH \prod_2^{3n} dp_j dq_j, \quad (2.17)$$

which is the form derived by the writer.⁴ It is equivalent to carrying out the indicated differentiation in (2.14) and is usually a more convenient starting point for calculations.

B. Ignorable Coordinates

In the absence of external forces, the Hamiltonian $H(\mathbf{p}, \mathbf{q})$ will be independent of the position of the center-of-mass \mathbf{R} and the Euler angles ω_L and ϕ_L , corresponding to rotation of the system about the total angular momentum L and its z -component M . We may also expect the chemical state of the system and hence the function $S(\mathbf{p}, \mathbf{q})$ to be independent of these coordinates. As a consequence, the corresponding Jacobians will all be zero, and (2.17) can be written

$$R(f, i) = \int \langle \rho \rangle \Gamma(f, i) dH d\mathbf{P} d\mathbf{R} dL d\omega_L dM d\phi_L, \quad (2.18)$$

where

$$\Gamma(f, i) = - \Gamma(i, f) = \int_{S(f, i)} \left(\sum_1^{3n-5} J_j / |J_1| \right) \prod_2^{3n-5} dp_j dq_j, \quad (2.19)$$

is the rate of flow of phase fluid across the surface $S(f, i)$ for fixed H , \mathbf{P} , \mathbf{R} , L , ω_L , M , and ϕ_L , and

$$\langle \rho \rangle = \Gamma^{-1}(f, i) \int_{S(f, i)} \rho \left(\sum_1^{3n-5} J_j / |J_1| \right) \prod_2^{3n-5} dp_j dq_j, \quad (2.20)$$

is the mean value of the density on the surface averaged with respect to the flow rate.

If additional constants of the motion (corresponding to ignorable coordinates) are known, the averaging of ρ may be restricted further. This will frequently be the case when the surface $S(f, i)$ is taken outside the region of strong interactions, and we shall consider some specific examples of this later. In general, however, no further reduction of expression (2.18) is possible without the introduction of specific assumptions concerning the Hamiltonian, the trial surface, or the density in the initial state, and (2.17) and (2.18) are the basic equations for estimating reaction rates.

C. Electronic Degeneracy

In deriving eqns. (2.17) and (2.18), we have tacitly assumed that the initial state of the system is non-degenerate. This is rarely the case, and there are usually several electronic configurations of the same energy which give rise to different interaction potentials. It is therefore necessary to multiply the rate for a given interaction potential (V_0) by the probability (f) that a system

in the initial state is moving on that particular potential curve. This may be expressed

$$f = g(V_0)/g(i), \quad (2.21)$$

where $g(V_0)$ is the electronic degeneracy associated with V_0 and $g(i)$ is the total degeneracy of the initial state. For simplicity we shall continue to omit this factor in our general considerations, but it must be taken into account in any explicit calculations.

D. General Rate Constant

To remove the dependence of the calculated rates on the concentration of the reactants, it is customary to express the results in terms of a reaction rate constant. The rate constant is defined as the reaction rate per unit volume divided by the product of the concentrations of the reactants. If the reaction is the result of the interaction of ν independent particles (where $\nu \leq n$), the reaction is said to be of order ν , and the rate constant is given by

$$k(f,i) = R(f,i)/V \prod_1^{\nu} [M_j], \quad (2.22)$$

where V is the normalization volume in configuration space and $[M_j]$ is the concentration of particles of type M_j in the initial state.

As a consequence of our assumption that the particles are independent, the density ρ in the initial state can be separated as a product of the densities ρ_j for the individual particles. Thus (2.4) for the total number of systems in the initial state can be written

$$N(i) = \int_{\Omega(i)} \left(\prod_1^{\nu} \rho_j \right) \prod_1^{3n} dp_j dq_j = V^{\nu} \prod_1^{\nu} [M_j]. \quad (2.23)$$

Combining eqns. (2.22) and (2.23), we obtain

$$k(f,i) = R(f,i) V^{\nu-1} / N(i) \quad (2.24)$$

as our expression for the rate constant of a reaction involving ν distinguishable particles proceeding at the rate $R(f,i)$ in a volume V . As can be seen from eqn. (2.6), $R(f,i)/N(i)$ has the dimensions of a reciprocal time, and hence (2.24) has the appropriate dimensions for a rate constant. For (2.24) to be valid, the calculated results must be independent of the normalization volume. As

will be seen below, this means that interactions between the particles must fall off sufficiently rapidly to make the reaction rate converge or that an artificial cut-off must be introduced.

E. Equilibrium Rate Constant

To calculate a bulk rate constant by means of the above equations, one must know the density ρ on the surface $S(f, i)$. For systems which are not in full thermodynamic equilibrium, this requires a solution of an appropriate master equation. However, in many systems which are out of chemical equilibrium, it may still be reasonable to suppose that the internal degrees of freedom of the reactants are in local equilibrium and can therefore be described by a Boltzmann distribution

$$\rho = \rho_0 e^{-H/kT}. \quad (2.25)$$

This assumption has been made in virtually all existing theories of bulk chemical reaction rates and leads to what may be called equilibrium rate constants.

Combining (2.25), (2.24), (2.17), and (2.4) and integrating over the center-of-mass coordinates, we obtain the following expression for the equilibrium rate constant:

$$k_e(f, i) = Q^{-1}(i) \int_{S(f, i)} e^{-E/kT} \left(\sum_1^{3n-3} J_j / |J_1| \right) dE \prod_2^{3n-3} dp_j dq_j, \quad (2.26)$$

where

$$Q(i) = V^{1-\nu} \int_{\Omega(i)} e^{-E/kT} \prod_1^{3n-3} dp_j dq_j, \quad (2.27)$$

is the classical partition function per unit volume for a system in the initial state and

$$E = H - P^2/2M \quad (2.28)$$

is the total energy in the center-of-mass. Note that the identification of $Q(i)$ as the partition function requires that the variations of $S(f, i)$ be so restricted that the value of $Q(i)$ does not differ appreciably from the usually accepted value of the partition function. This criterion, in fact, determines the acceptable range of surfaces which may be used.

III. COMPARISON WITH CONVENTIONAL THEORIES

Before proceeding to the newer and more unique applications of the variational theory, it is instructive to investigate its relationship to some older and more familiar theories of chemical reaction rates. Almost all of these are based on the assumption of a Boltzmann distribution for the reactants, and of trial surfaces separating reactants and products that depend only on the coordinates in configuration space. The differences (which can be substantial) between various theories are due primarily to the particular trial surfaces chosen, and it is here that the variational theory provides both a connecting link and a criterion for selection.

A. Unimolecular Decay Theory

In the theory of unimolecular decay as developed by Slater,⁵ it is assumed that an activated molecule will dissociate when a particular coordinate q_1 reaches a high value q . Thus the trial surface is defined by

$$S = q_1 - q = 0, \quad (3.1)$$

and the only nonvanishing Jacobian in eqn. (2.26) is

$$J_1 = \partial E / \partial p_1 = q_1. \quad (3.2)$$

Substituting (3.1) and (3.2) into (2.26) and (2.27), we obtain the high-pressure rate constant

$$k^\infty = Q^{-1} \int_{q_1 > 0} e^{-E^*/kT} q_1 dp_1 \prod_2^{3n-3} dp_j dq_j, \quad (3.3)$$

where

$$Q = \int e^{-E/kT} \prod_1^{3n-3} dp_j dq_j \quad (3.4)$$

and E^* is the energy on the surface $q_1 = q$. Equation (3.3) is just Pelzer's formula in the general form derived in Chapter 9 of Slater's book.

B. Theory of Absolute Reaction Rates

In the theory of absolute reaction rates as developed by Eyring and his collaborators,⁶ it is assumed that a chemical reaction can

be described as a flow of representative points over a saddle point in the potential energy of the system from a valley representing the reactants to one representing the products. A reaction coordinate q_1 parallel to the bottom of the valley is defined, and the flow rate through a surface perpendicular to q_1 located at the saddle point is then calculated, a Boltzmann distribution for the reactants being assumed. A variational version of the theory has also been proposed by Horiuti,³ who points out that the best location for the surface is not necessarily at the saddle point but rather at the point where the flow rate through the surface is a minimum.

Following Horiuti, we introduce a surface $S(f,i)$ between reactants and products that spans the potential energy valley. We then chose as our coordinate system an orthogonal curvilinear set of q 's with q_1 perpendicular to $S(f,i)$. Under these conditions the energy of the system is

$$E = p_1^2/2\mu_1 + E^*, \quad (3.5)$$

where p_1 and μ_1 are respectively the momentum and reduced mass corresponding to q_1 , and the only non-vanishing Jacobian in (2.26) is

$$J_1 = \partial E/\partial p_1 = q_1. \quad (3.6)$$

Substituting (3.5) and (3.6) in (2.26) and integrating over p_1 , we obtain

$$k^E = kTQ^{-1} \int_{S(f,i)} e^{-E^*/kT} \prod_2^{3n-3} dp_j dq_j, \quad (3.7)$$

where Q is given by (2.27). The integral in (3.7) is just the classical partition function of the system constrained to the surface $S(f,i)$; i.e.

$$Q^* = \int_{S(f,i)} e^{-E^*/kT} \prod_2^{3n-3} dp_j dq_j. \quad (3.8)$$

If we now "quantize" our system and let $Q^* = Q_q^* h^{3n-4}$ and $Q = Q_q h^{3n-3}$, equation (2.35) takes the familiar form

$$\mathbf{3:7} \quad k^E = (kT/h) \cdot Q_q^*/Q_q \quad (3.9)$$

associated with the theory of absolute reaction rates.

As shown by Horiuti, the surface which minimizes the rate constant k^E must satisfy the variational equation

$$\delta Q^* = 0, \quad (3.10)$$

which leads immediately to the condition

$$(kT)^{-1} \partial E^* / \partial q_1 = \sum_2^{3n-3} \rho_j^{-1}, \quad (3.11)$$

where the ρ_j 's are the principal radii of curvature of the surface $S(f, i)$. If $S(f, i)$ is a Cartesian plane, eqn. (3.11) becomes

$$\partial E^* / \partial q_1 = \partial V_0^* / \partial q_1 = 0,$$

which locates the surface at the saddle point, as in the Eyring theory. It is not clear, in general, how much the rate can be reduced by employing more complicated surfaces, but Horiuti has made estimates which indicate that, in cases where the barrier height is not large compared to kT , effects due to curvature could be significant.

C. Available Energy Theory

The available energy theory is based on the work of Lindemann⁷ and Hinshelwood.⁸ The basic assumption of this theory⁹ is that a reaction can occur only for those collisions in which sufficient energy is "available" in some number, v , of quadratic terms in the energy of the reactants in the center-of-mass system. If all the terms in the energy are included, this certainly gives an upper limit to the reaction rate. The difficulty is that this usually leads to a gross overestimate of the rate, and v must be restricted to a smaller number. At this point the theory becomes reduced to a sort of guessing game, in which even for simple molecules it is possible to obtain results that vary by orders of magnitude depending on the choice of v . In spite of this objection, the theory is useful for correlating experimental data and setting limits for unknown rates of complex reactions.

The appropriate trial surface for this theory is defined by the constraints

$$S = r - a = 0 \quad (3.12)$$

and

$$p^2/2\mu + \sum_2^v \beta_j \lambda_j^2 \geq D, \quad (3.13)$$

where a is an assumed collision diameter, r and p are the radial separation and conjugate momentum, μ is the reduced mass for the collision, x_j is a generalized coordinate, β_j is the coefficient of x_j^2 in the energy equation, and D is the energy required for a reaction. In addition to (3.12) and (3.13), we also have the energy equation

$$E = p^2/2\mu + \sum_2^{6n-7} \beta_j x_j^2. \quad (3.14)$$

Note that in (3.14) we have tacitly assumed that the interaction potential at $r = a$ may be neglected. With these constraints, the only non-vanishing Jacobian in (2.26) is $J_1 = \partial E/\partial p = \dot{r}$, and the available energy rate constant can be expressed

$$k_d^A = Q^{-1} \int e^{-E/kT} dE \prod_2^{6n-7} dx_j, \quad (3.15)$$

with

$$Q = V^{-1} \int e^{-E/kT} dp dr \prod_2^{3n-3} dp_j dq_j. \quad (3.16)$$

Expressions (3.15) and (3.16) can easily be integrated by using (3.12), (3.13), and (3.14), and this leads to the well-known result

$$k_d^A = \pi a^2 \left(\frac{8kT}{\pi\mu} \right)^{\frac{1}{2}} \Gamma^{-1} \left(\frac{v+1}{2} \right) \int_{D/kT}^{\infty} e^{-x} x^{(v-1)/2} dx, \quad (3.17)$$

which for $kT/D \ll 1$ becomes approximately

$$k_d^A \approx \pi a^2 \left(\frac{8kT}{\pi\mu} \right)^{\frac{1}{2}} \Gamma^{-1} \left(\frac{v+1}{2} \right) \left(\frac{D}{kT} \right)^{(v-1)/2} e^{-D/kT}, \quad (3.18)$$

where Γ is the Γ -function.

In concluding this Section, we note that the above calculation does not represent a rigorous application of the variational theory because the surface $r = a$ does not completely divide the reactants from the products unless the interaction potential is assumed to be sharply cut off at a . That is to say, our surface has "holes" in it through which the systems can "leak" without contributing to the integral in (3.15). We cannot claim, therefore, that (3.17) is a rigorous upper limit and vary our a to obtain a minimum rate. If we did we would, of course, get zero for an answer. A further criticism of (3.17) which becomes important at high temperatures

is that integrals over the internal degrees of freedom of the reactants have all been extended to infinity, and no account is taken of the fact that finite potentials are involved.

D. Statistical Theory

In the opinion of the writer, the most serious criticism of the available energy theory as outlined above is that it fails to include explicitly a factor giving the reaction probability when the energy is available. This omission is responsible for many of the apparent difficulties and inconsistencies which arise in the practical application of the theory and, in 1958, led the writer to propose a statistical theory¹⁰ of reaction rates in which the reaction probability was assumed to be proportional to the rate of flow of phase fluid across the boundaries of a collision complex into the product state. Before this, the same assumption was used by Hart, Gray, and Guier¹¹ in order to estimate branching ratios for atomic excitation by electron impact. Recently, a similar quantum-mechanical theory was proposed by Light,¹² that in its original form failed to satisfy detailed balancing and was subsequently revised by Pechukas and Light¹³ to a form representing a special case of the writer's more general theory.¹⁰

Fundamentally, the statistical theory is based on scattering theory in the strong-coupling approximation,¹⁴ and a derivation of the theory from first principles has been given by Eu and Ross.¹⁵ It is also closely related to the compound nucleus theory of nuclear reactions¹⁴ and Fermi's statistical theory of meson production.¹⁶

To obtain an expression for the statistical rate constant, we postulate the formation of a collision complex Ω^* through which the reaction passes. Let $S(f,*)$ be that part of the surface of the collision complex through which the reaction products enter the final state f . Then the partial rate at which products are formed in this state with fixed total energy H , momentum \mathbf{P} , and angular momentum L , obtained from (2.18), is $\langle \rho \rangle_f \Gamma(f,*)$, and the probability of forming this state is exactly

$$P_f(H, \mathbf{P}, L) = \langle \rho \rangle_f \Gamma(f,*) / \sum_j \langle \rho \rangle_j \Gamma(j,*) \quad (3.19)$$

Note that in writing (3.19), we have made the assumption that the reaction probability is independent of the position of the complex and the orientation of the total angular momentum.

The basic assumption of the statistical theory is that the mean value of the density $\langle \rho \rangle$ on the surface of the collision complex is the same for all product channels. With this assumption, (3.19) becomes

$$P_f(H, \mathbf{P}, L) = \Gamma(f, *) / \sum_j \Gamma(j, *), \quad (3.20)$$

which is independent of the manner in which the collision complex was formed and depends only on the location of its boundaries and the Hamiltonian H determining the flow field of the phase fluid. The statistical rate constant may now be obtained by inserting (3.20) into (2.18), integrating over the ignorable coordinates \mathbf{R} , and substituting the result into (2.24). This gives the expression

$$k^S = \frac{V^v}{N(i)} \int_{S^*(*, i)} \langle \rho \rangle_i \frac{\Gamma(f, *) \Gamma(i, *)}{\sum_j \Gamma(j, *)} dH d\mathbf{P} dL d\omega_L dM d\phi_L, \quad (3.21)$$

which is equivalent to equation (5) of the writer's previous paper.¹⁰

We now consider the important special case in which the collisions are binary, and the boundary of the collision complex is defined by the equation

$$S = r - z(l) = 0, \quad (3.22)$$

where r and l are the radial separation and orbital angular momentum of the reactants, and $z(l)$ is the position of the maximum in the effective potential $V'(r)$ governing the radial motion of the reactants. We further assume that the interactions are negligible for $r > z$, so that the internal energy $E'(l', \alpha)$ and rotational angular momentum l' of the molecules are constants of the motion.

The Hamiltonian can then be written

$$H = P^2/2M + E'(l', \alpha) + E_j, \quad (3.23)$$

where

$$E_j = p^2/2\mu_j + l^2/2\mu_j r^2 + V_j(r) \quad (3.24)$$

is the relative kinetic energy of the collision partners, p is the radial momentum conjugate to r , μ_j is the reduced mass for the collision, and α stands for the set of action variables

$$\alpha_k = \oint p_k dq_k \quad (3.25)$$

required to complete the description of the reactants or products in the state j .

For the surface defined by (3.22) and the Hamiltonian (3.23), the only non-vanishing Jacobian in (2.19) and (2.20) is $J_1 = \partial H / \partial p = \dot{p} / \mu$, and the mean density $\langle \rho \rangle_i$ and flow rate $\Gamma(j, *)$ in (3.21) can be written explicitly

$$\langle \rho \rangle_i = \Gamma^{-1}(i, *) \int_{S(i, *)} \rho d l d \omega d l' d \omega' \prod_1^{3n-8} d \alpha_k \quad (3.26)$$

and

$$\Gamma(j, *) = \int_{S(j, *)} d l d \omega d l' d \omega' \prod_1^{3n-8} d \alpha_k, \quad (3.27)$$

where ω and ω' are the Euler angles corresponding to rotation about l and l' , and the surface $S(j, *)$ is defined by the set of constraints

$$r = z, \quad \dot{p} > 0, \quad l + l' > L > |l - l'|. \quad (3.28)$$

Note that (3.26) and (3.27) contain implicitly the fact that the Jacobian of the transformation from m, ϕ, m', ϕ' to L, ω_L, M, ϕ_L is unity, where m and m' are the z -components of l and l' , and ϕ and ϕ' are the corresponding Euler angles corresponding to rotation about the z -axis. We may also obtain an explicit expression for $N(i)$ from (2.4):

$$N(i) = V \int \rho d \mathbf{P} d \mathbf{p} d \mathbf{r} d l' d \omega' d m' d \phi' \prod_1^{3n-8} d \alpha_{ik}, \quad (3.29)$$

where we have integrated over $d\mathbf{R}$.

To compare these results directly with those of Pechukas and Light, we require the differential rate constant $k^s(H, E_i, l'_i, \alpha_i, l'_f, \alpha_f)$ for reactions having fixed total energy H and relative kinetic energy E_i in the initial state, and specified values of rotational angular momentum l' and action α in the initial and final states. This is easily obtained from our integral expressions by simply deleting these variables, and we find, on combining (3.21), (3.26), (3.27), and (3.29) and integrating over angles,

$$k^s(H, E_i, l'_i, \alpha_i, l'_f, \alpha_f) = \frac{\pi v_i}{(2\mu_i E_i) 2l'_i} \int dL dM \frac{\gamma(f, *) \gamma(i, *)}{\Gamma(*)}, \quad (3.30)$$

where $v_i = (2E_i/\mu_i)^{1/2}$ is the relative velocity for the collision,

$$\gamma(j,*) = \int_{S(j,*)} dl \quad (3.31)$$

is the differential flow rate of phase fluid into the state j , and the surface $S(j,*)$ is defined by (3.28) together with (3.23) and (3.24).

To "quantize" the system, it is simply necessary to measure angular momentum in units of \hbar , action in units of h , and convert integrals to sums. Thus (3.30) becomes

$$k^s(H, E_i, l'_i, \alpha_i, l'_j, \alpha_j) = \frac{\pi \hbar^2 v_i}{(2\mu_i E_i)(2l'_i + 1)} \cdot \sum_{L, M} \frac{\gamma(f,*)\gamma(i,*)}{\Gamma(*)} \quad (3.32)$$

where

$$\gamma(j,*) = \sum_l X_l(L, E_j, l'_j), \quad (3.33)$$

$$\Gamma(*) = \sum_{l'_j, \alpha_j} \gamma(f,*), \quad (3.34)$$

and the characteristic function X_l determined by the constraints (3.28), (3.23), and (3.24) is

$$X_l = \begin{cases} 1 : l + l'_j \geq L \geq |l - l'_j|, & E_j \geq V'_j(z) \\ 0 : \text{otherwise} \end{cases} \quad (3.35)$$

Since the cross section σ for a reaction is simply k/v , eqn. (3.32) is identical with eqn. (7) of Pechukas and Light.¹³

It is interesting (and comforting) to note that while the results obtained by the writer and Pechukas and Light are the same, the methods used to arrive at them could hardly be more different. Pechukas and Light start with a quantum-mechanical formulation and introduce an arbitrary "measure," the character of which is then determined by detailed balancing arguments. This leaves the physical interpretation of the "measure" somewhat obscure. On the other hand, the writer starts with a classical approach and immediately identifies the "measure" as the rate of flow of phase fluid into the various states. This gives a clear physical meaning to the theory. In this connection it may be observed that it was the omission of the flow velocity which led to the detailed balancing failure found in Light's original paper.¹² The same error was also made by Horie and Kasuga.¹⁷

The conditions under which the statistical theory may actually be valid in chemical reactions are not yet clear. In the writer's work on three-body atom recombination,¹⁰ it has been found unsatisfactory. On the other hand, Pechukas and Light have reported some success in applying the theory to exchange reactions involving ionic molecules. There is also the possibility that the theory may be a reasonable approximation for reactions involving polyatomic molecules. In any case, the theory is an improvement over the available energy theory if only because it satisfies detailed balancing.

IV. THREE-BODY RECOMBINATION AND DISSOCIATION

One of the most important applications of the variational theory which has been made to date is to the problem of three-body recombination and dissociation of atoms and ions. This problem has been treated by a variety of methods, and we shall review several of them to illustrate how the calculations are made and to permit a comparison of the results. For the sake of uniformity and to remove the strong dependence on the Boltzmann factor, we shall give our results in terms of three-body recombination rate constants. The four rate constants that we shall consider in detail are the (1) available energy, (2) three-body collision, (3) Wigner, and (4) barrier-rate constants. We shall omit detailed consideration of the statistical rate constant¹⁰ because the calculations are rather complicated, and the theory is asymptotic to the available energy and three-body collision theories at high and low temperatures, respectively, and varies smoothly in between.

A. The Model

All of our calculations will be made for a system of three distinguishable particles. We assume that the motion can be described classically and that the full three-body interaction potential V_0 is known. We further assume in the case of atoms and molecules that electronic transitions do not occur during a collision, so that V_0 is invariant. The canonical coordinates $p_{12}, r_{12}, l_{12}, \omega_{12}, m_{12}, \phi_{12}$ will be used to describe the relative motion of particles 1 and 2 and the coordinates $p_3, r_3, l_3, \omega_3, m_3, \phi_3$ to describe the motion of

particle 3 with respect to the center-of-mass of the "molecule" composed of particles 1 and 2. In this set p and r denote the radial momentum and separation, l and ω the angular momentum and conjugate Euler angle, and m and ϕ the z -component of l and conjugate Euler angle. These coordinates, which are shown in Fig. 1, are closely related to the Delaunay elements¹⁸ used in astronomy and in the old Bohr quantum theory.

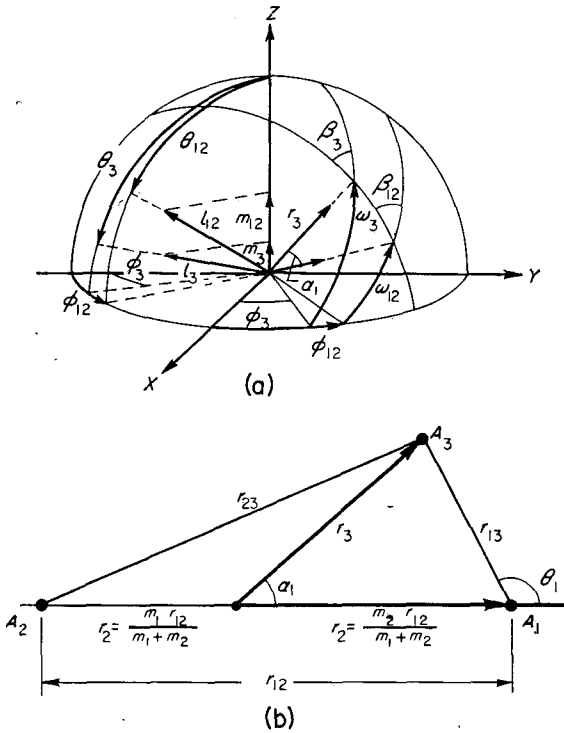


Fig. 1. Coordinates used to describe the relative motion of three particles.

The Hamiltonian in the center-of-mass system can now be written

$$E = E_{12} + p_3^2/2\mu_3 + l_3^2/2\mu_3 r_3^2 + V_3, \quad (4.1)$$

where

$$E_{12} = p_{12}^2/2\mu_{12} + l_{12}^2/2\mu_{12} r_{12}^2 + V_{12} \quad (4.2)$$

is the energy of the molecule,

$$V_3 = V_0 - V_{12} \quad (4.3)$$

is the interaction potential, μ_3 is the reduced mass for the collision, and V_{12} and μ_{12} are the interaction potential and reduced mass for the molecule.

To describe an attractive interaction between atoms, we shall use the Morse potential

$$V_M(r) = D[(1 - e^{-\beta(r-r_e)})^2 - 1]. \quad (4.4)$$

The corresponding "effective potential" governing the radial motion of the molecule is

$$V'(r) = l^2/2\mu r^2 + V_M(r). \quad (4.5)$$

The general characteristics of the "effective potential" for a sharply cut-off interaction such as the Morse interaction are shown

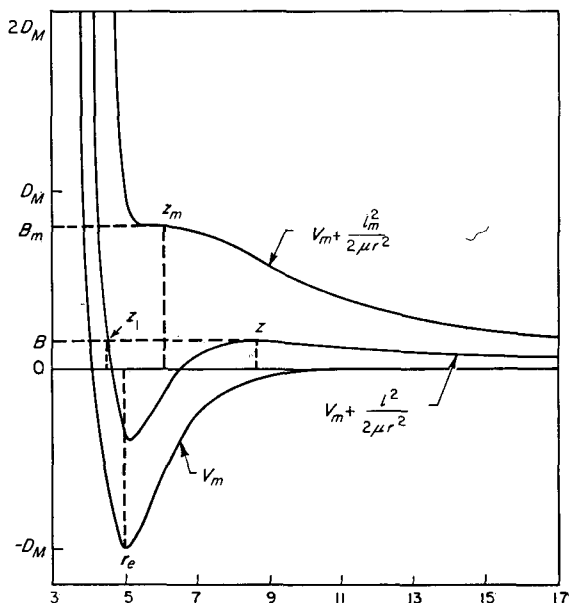


Fig. 2. General characteristics of the effective potential for a Morse interaction.

by the curves in Fig. 2. If l is not too large, there is a relative maximum, the rotational barrier, at a radius z given by

$$(dV'/dr)_z = (dV_M/dr - l^2/\mu r^3)_z = 0. \quad (4.6)$$

If we let B denote the height of the rotational maximum, then it can easily be shown, by using (4.5) and (4.6), that

$$dB/dl^2 = (2\mu z^2)^{-1}. \quad (4.7)$$

This equation has been found very useful in dealing with collision problems.

As in our previous calculations, we shall assume that the internal state of the system can be described by a Boltzmann distribution $\rho = \rho_0 \exp(-E/kT)$ and compute equilibrium rate constants.

B. Available Energy Rate

We shall first calculate a rate constant for atomic recombination based on the available-energy theory described in Section III C. However, in our present calculation, we shall use a somewhat more realistic trial surface which takes into account the finite depth of the Morse potential. This surface $S(A)$ is defined by

$$S = r_3 - a = 0, \quad (4.8)$$

where a is a characteristic collision diameter that may be taken roughly as the radius at which the magnitude of the interaction potential V_3 in (4.1) is equal to kT . In addition we require that the molecule be bound in the initial state, so that

$$E_{12} \leq B \leq B_m, \quad r_{12} \leq z, \quad (4.9)$$

where B_m is the maximum value of B ; we require further that the energy to dissociate be available, so that

$$E \geq 0. \quad (4.10)$$

The equilibrium rate constant for this surface can now be obtained from (2.26) and after integration over angles can be written

$$k_r^A = f(2\pi)^4 Q^{-1} \int_{S(A)} e^{-E/kT} \tau_{12} dE_{12} dl_1^2 dl_2^2 dE, \quad (4.11)$$

where

$$f = g_{12}/g_1g_2 \quad (4.12)$$

is the electronic degeneracy factor (2.21),

$$Q = (2\pi\mu_{12}kT)^{3/2}(2\pi\mu_3kT)^{3/2}, \quad (4.13)$$

and the period τ_{12} for a rotating Morse oscillator can be approximated

$$\tau_{12} \approx [2\pi^2\mu_{12}/\beta^2(B - E_{12})]^{1/2}. \quad (4.14)$$

The major contribution to the integral in (4.11) comes from the region of phase space in the vicinity of the minimum in the Morse potential, and a very satisfactory approximation to (4.11) can be obtained by setting r_{12} in (4.2) equal to r_e . This gives

$$k_r^A = f\pi a^2 \left(\frac{4\pi r_e^2}{\beta}\right) \left(\frac{2D}{\mu_3}\right)^{1/2} \cdot \frac{8}{15} \cdot \frac{D}{kT} \left(\frac{D}{kT} + 5\right). \quad (4.15)$$

This expression for the available energy recombination rate constant is valid for all values of kT/D and is not restricted to $kT/D \ll 1$ as is the conventional available-energy recombination rate constant obtained by detailed balancing from (3.17). A plot of k_r^A as a function of kT is shown in Fig. 3.

C. Three-body Collision Rate

Although a three-body collision may occur in several ways, for our present purpose we shall define it as a collision of particle 3 with a pair of free particles 1 and 2 orbiting at a separation r_{12} less than the radius of the rotational maximum z . The corresponding trial surface $S(T)$ is determined by the constraints

$$S = r_3 - a = 0, \quad r_{12} \leq z, \quad E_{12} \geq B \quad (4.16)$$

with the auxiliary conditions

$$E \geq 0, \quad B \leq B_m, \quad (4.17)$$

and the three-body recombination rate constant obtained from (2.26) after integrating over angles is

$$k_r^T = f(2\pi)^4(2\mu_3Q)^{-1} \int_{S(T)} e^{-E/kT} \tau_{12} dE_{12} dl_{12}^2 dl_3^2 dp_3^2, \quad (4.18)$$

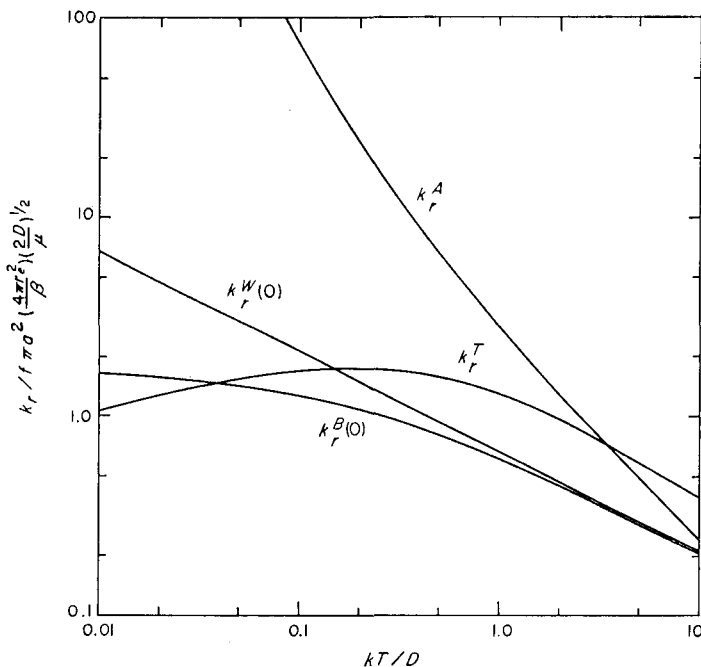


Fig. 3. Dimensionless comparisons of available energy k_r^A , three-body collision k_r^T , Wigner $k_r^W(0)$, and barrier $k_r^B(0)$ recombination rate constants for a Morse potential with $\beta r_e = 3$. Note that k_r^A and k_r^T scale as $\mu_3^{-1/2}$, while $k_r^W(0)$ and $k_r^B(0)$ scale as $\mu_{12}^{-1/2}$. See text for definition of parameters.

where Q is given by (4.13) and the effective collision time τ_{12} can be approximated

$$\tau_{12} = [2\mu_{12}/\beta^2(E_{12} - B)]^{1/2}. \quad (4.19)$$

The integration of (4.18) with respect to dl_{12}^2 , dp_3^2 , and dE_{12} can be carried out exactly and yields

$$k_r^T = \frac{f(2\pi a)^2}{\beta\mu_{12}} \left(\frac{2}{\pi\mu_3 kT} \right)^{1/2} \int e^{-B/kT} dl_{12}^2. \quad (4.20)$$

To carry out the remaining integration, we substitute the variable z for l_{12} using (4.7), so that (4.20) becomes

$$k_r^T = \frac{f(2\pi a)^2}{\beta} \left(\frac{8}{\pi\mu_3 kT} \right)^{1/2} \int e^{-B/kT} z^2 \frac{dB}{dz} dz. \quad (4.21)$$

We now observe that, for sharply cut-off potentials such as the Morse potential, the factor $(dB/dz) \exp(-B/kT)$ in the integrand of (4.21) has a strong maximum at the position z_2 , defined by

$$(d/dz)[(dB/dz) \exp(-B/kT)]_{z_2} = 0. \quad (4.22)$$

Setting $z^2 = z_2^2$ in the integrand of (4.21), the remaining integration can be carried over dB and gives

$$k_r^T = f\pi a^2 \left(\frac{4\pi z_2^2}{\beta}\right) \left(\frac{2D}{\mu_3}\right)^{\frac{1}{2}} \frac{2}{\sqrt{\pi}} \left(\frac{kT}{D}\right)^{\frac{1}{2}} (1 - e^{-E_m/kT}). \quad (4.23)$$

It may be noted that this expression for the three-body collision rate constant is substantially identical to that obtained from Rice's theory¹⁹ of dissociation by detailed balancing.

A plot of the three-body collision rate constant is shown in Fig. 3, and it is seen to be smaller than the available-energy rate constant for all values of $kT/D < 3$. Thus the available-energy rate constant cannot be regarded as a good approximation in this range in spite of the appealing fact that it gives a negative temperature coefficient more nearly in agreement with experiments.

For $kT/D > 3$, however, the available-energy theory does give a lower limit than the three-body collision theory. The physical reason for this is that, for small values of kT/D , the phase space available to three free particles is much smaller than that available to two, so that decay of the collision complex into three particles becomes the rate-limiting step. For large kT/D the reverse is true, and two-particle decay is the rate-limiting step. The statistical theory¹⁰ of reaction rates automatically takes this into account and, as already mentioned, provides a smooth transition between the two expressions (4.15) and (4.23). It should be noted that, strictly speaking, neither of these expressions is a rigorous upper limit to the true rate constant because the trial surfaces used are "leaky". Nevertheless, they are sufficiently good for practical purposes, and the smaller of the two should give the best approximation to the true rate constant.

D. Wigner Rate

Wigner² obtained a rigorous upper limit to the three-body recombination rate constant by calculating the flow of molecules through the surface $E_{12} = 0$. This is the first of the surfaces

considered that divides molecules from free atoms without "leaks". It is also the first to depend on the momentum coordinates and, therefore, to involve explicitly the form of the interaction potential V_3 .

In our present calculation we shall use a slightly more general trial surface $S(W)$ defined by

$$S = E_{12} + E_0 = 0, \quad E \geq -E_0, \quad (4.24)$$

where E_0 is a constant that we shall later vary to obtain the minimum rate. For this surface there are two non-vanishing Jacobians in our general expression (2.26) for the rate constant. These are

$$J_1 = \frac{\partial E}{\partial p_{12}} \cdot \frac{\partial E_{12}}{\partial r_{12}} - \frac{\partial E}{\partial r_{12}} \cdot \frac{\partial E_{12}}{\partial p_{12}} = -\frac{p_{12}}{\mu_{12}} \cdot \frac{\partial V_3}{\partial r_{12}} \quad (4.25a)$$

and

$$J_2 = -\frac{\partial E}{\partial \omega_{12}} \cdot \frac{\partial E_{12}}{\partial l_{12}} = -\frac{l_{12}}{\mu_{12} r_{12}^2} \cdot \frac{\partial V_3}{\partial \omega_{12}} \quad (4.25b)$$

Substituting (4.25) into (2.26) we obtain

$$\begin{aligned} k_r^W(E_0) = fQ^{-1} \int_{S(W)} e^{-E/kT} & \left(\frac{p_{12}}{|p_{12}|} \frac{\partial V_3}{\partial r_{12}} + \frac{\gamma_W}{r_{12}} \frac{\partial V_3}{\partial \omega_{12}} \right) \\ & \times dr_{12} dl_{12} d\omega_{12} dm_{12} d\phi_{12} dp_3 dr_3 dl_3 d\omega_3 dm_3 d\phi_3 \end{aligned} \quad (4.26)$$

where

$$\gamma_W = r_{12} \frac{\partial p_{12}}{\partial l_{12}} = [2\mu_{12} r_{12}^2 (-E_0 - V_{12}) / l_{12}^2 - 1]^{-1/2} \quad (4.27)$$

and Q is given by (4.13).

To integrate (4.26), it is convenient to make the transformation

$$d\omega_{12} dm_{12} d\phi_{12} = l_{12} d\beta_{12} d\beta_3 d\cos\alpha, \quad (4.28)$$

where β_{12} , β_3 , and α are the angles shown in Fig. 1 which determine the relative position and velocities of the particles. Equation (4.26) can then be written

$$\begin{aligned} k_r^W(E_0) = fQ^{-1} \int_{S(W)} e^{-E/kT} & \left(\frac{p_{12}}{|p_{12}|} \cdot \frac{\partial V_3}{\partial r_{12}} - \frac{\gamma_W \cos\beta_{12}}{r_{12}} \cdot \frac{\partial V_3}{\partial \alpha} \right) l_{12} \\ & \times dp_3 dl_3 d\omega_3 dm_3 d\phi_3 d\beta_3 d\beta_{12} dl_{12} dr_{12} dr_3 d\cos\alpha \end{aligned} \quad (4.29)$$

and the integration over the first eight variables can be carried out conveniently in the order given. This yields

$$k_r^W(E_0) = \frac{f8\pi}{(kT)^2} \left(\frac{2kT}{\mu_{12}}\right)^{\frac{1}{2}} \int_{-E_0 > V_{12}} e^{(E_0 - V_3)/kT} \left[\left(\frac{\partial V_3}{\partial r_{12}}\right)^2 + \left(\frac{1}{r_{12}} \frac{\partial V_3}{\partial \alpha}\right)^2 \right]^{\frac{1}{2}} \\ \times \Gamma\left(\frac{3}{2}, \frac{|V_3| - V_3}{2kT}\right) (-E_0 - V_{12}) r_{12}^2 dr_{12} r_3^2 dr_3 d \cos \alpha, \quad (4.30)$$

where

$$\Gamma(n+1, x) = \int_x^\infty y^n e^{-y} dy \quad (4.31)$$

is the incomplete Γ -function.

The expression in square brackets in (4.30) can be recognized as the magnitude of the force acting to change the energy of the molecule. The two terms correspond to vibrational and rotational transitions, and we note that, if the interaction potential V_3 is assumed to be spherically symmetric, there will be no contribution due to rotational transitions.

1. *Atomic recombination.* To proceed further we must specify the interaction potential V_3 . For the case of atomic recombination, we assume as a first approximation

$$V_3 \approx V_{13}(r_{13}) + V_{23}(r_{23}) \geq 0 \quad (4.32)$$

and observe that, if V_{13} and V_{23} are sufficiently steep, the integrand in (4.30) will possess a strong maximum on two spherical shells with radii a_{13} and a_{23} defined by

$$(d/dr_{13})[(dV_{13}/dr_{13}) \exp(-V_{13}/kT)]_{a_{13}} = 0 \quad (4.33a)$$

and

$$(d/dr_{23})[(dV_{23}/dr_{23}) \exp(-V_{23}/kT)]_{a_{23}} = 0. \quad (4.33b)$$

This "dumbbell model" permits one to divide the integral in (4.30) into two parts corresponding to integration over the two ends of the dumbbell, so that

$$k_r^W(E_0) = k_{r_1}^W(E_0) + k_{r_2}^W(E_0), \quad (4.34)$$

where

$$k_{r_1}^W(E_0) = \frac{f8\pi}{(kT)^2} \left(\frac{\pi kT}{2\mu_{12}}\right)^{\frac{1}{2}} \left(\frac{m_2}{m_1 + m_2}\right) \int_{-E_0 > V_{12}, \theta_{1m} > \theta_1} (-E_0 - V_{12}) \\ \times \frac{dV_{13}}{dr_{13}} e^{(E_0 - V_{13})/kT} r_{12}^2 dr_{12} r_{13}^2 dr_{13} d \cos \theta_1, \quad (4.35)$$

and we have made the transformation

$$r_3^2 dr_3 d \cos \alpha = r_{13}^2 dr_{13} d \cos \theta_1. \quad (4.36)$$

The angle θ_1 is shown in Fig. 1(b), and θ_{1m} is defined by

$$\cos \theta_{1m} = (a_{23}^2 - a_{13}^2 - r_{12}^2) / 2a_{13}r_{12}. \quad (4.37)$$

$k_{r_2}^W(E_0)$ is given by the corresponding expressions with the subscripts 1 and 2 interchanged.

The integration over $dr_{13} d \cos \theta_1$ may now be carried out approximately by setting $r_{13}^2 = a_{13}^2$ in the integrand of (4.35), and we find

$$k_r^W(E_0) = f4\pi \left(\frac{2\pi\mu_{12}}{kT} \right)^{\frac{1}{2}} e^{E_0/kT} \int_{-E_0 > V_{12}} (-E_0 - V_{12}) r_{12}^2 \\ \times [a_{13}^2 m_1^{-1} (1 - \cos \theta_{1m}) + a_{23}^2 m_2^{-1} (1 - \cos \theta_{2m})] dr_{12}, \quad (4.38)$$

where we have added $k_{r_1}^W(E_0)$ and $k_{r_2}^W(E_0)$. This is equivalent to the result obtained by Wigner.²

The remaining integration over dr_{12} may also be carried out approximately by observing that for a Morse potential (4.4) the factor $(-E_0 - V_{12})$ has a strong maximum at $r_{12} = r_e$. Expanding the integrand about this point, we obtain

$$k_r^W(E_0) = f\pi a^2 \left(\frac{4\pi r_e^2}{\beta} \right) \left(\frac{2D}{\mu_{12}} \right)^{\frac{1}{2}} \frac{4}{3\sqrt{\pi}} \left(\frac{D}{kT} \right)^{\frac{1}{2}} \left(1 - \frac{E_0}{D} \right)^{3/2} e^{E_0/kT}, \quad (4.39)$$

where

$$a^2 = \frac{m_2 a_{13} [(a_{13} + r_e)^2 - a_{23}^2] + m_1 a_{23} [(a_{23} + r_e)^2 - a_{13}^2]}{2(m_1 + m_2)r_e} \quad (4.40)$$

is the square of an effective collision radius.

For $E_0 \ll D$, $k_r^W(E_0)$ is an increasing function of E_0 , and since E_0 must be greater than zero to avoid a "hole" in the trial surface, the best choice of E_0 is the one made by Wigner, namely, zero, and (4.39) becomes simply

$$k_r^W(0) = f\pi a^2 \left(\frac{4\pi r_e^2}{\beta} \right) \left(\frac{2D}{\mu_{12}} \right)^{\frac{1}{2}} \frac{4}{3\sqrt{\pi}} \left(\frac{D}{kT} \right)^{\frac{1}{2}}. \quad (4.41)$$

A plot of this expression is shown in Fig. 3. For $\mu_{12} \sim \mu_3$, the Wigner rate is smaller than the available energy rate over the entire temperature range shown and smaller than the three-body

collision rate for $kT/D \gtrsim .15$. For light third bodies, i.e., $\mu_3 \ll \mu_{12}$, the Wigner rate will be the best approximation to somewhat/lower temperature, but the three-body collision rate will still give the smallest limit over most of the range $kT/D < 0.1$ where experiments have been performed.

2. *Electron recombination.* A calculation similar to that described above has also been made by Makin and Keck²⁰ for the three-body electron recombination process $A^+ + e + e \rightarrow A + e$. In this case the integral in (4.29) diverges linearly with r_3 owing to the long range of the Coulomb forces involved, and a cut-off must be introduced. Since the energy transfer is, in general, small for collisions in which the product of the angular frequency ω of an oscillator and the collision time τ is large, a reasonable cut-off is $\omega\tau = 1$. The integration of (4.29) may then be carried out with the aid of a computer and the results represented by an expression of the form

$$k_r^e(E_0) = \frac{3\pi}{4} \left(\frac{e}{kT}\right)^5 \left(\frac{8kT}{\pi m_e}\right)^{\frac{1}{2}} \left(\frac{kT}{E_0}\right)^4 (e^{8E_0/5kT} + 5e^{E_0/kT}). \quad (4.42)$$

This rate constant has a minimum at $E_0/kT = 5/2$, which may be interpreted physically as giving the location of the rate-limiting step or "bottleneck" in the electron cascade toward the ground state. Similar theoretical results have been obtained by Bates, Kingston, and McWhirter,²¹ and supporting experimental evidence is provided by the work of Hinnov and Hirshberg.²²

E. Barrier Rate Constant

The barrier rate constant was introduced by the writer⁴ to take into account the effects of the rotational barrier. It involves passage of a molecule through a trial surface a fixed energy E_0 below the top of the rotational barrier. This surface $S(B)$ is defined by the constraints

$$S = E_{12} - B_{12} + E_0 = 0, \quad E \geq -E_0, \quad (4.43)$$

and gives two non-vanishing Jacobians in (2.26), namely:

$$J_1 = \frac{\partial E}{\partial \dot{p}_{12}} \cdot \frac{\partial E_{12}}{\partial r_{12}} - \frac{\partial E_{12}}{\partial \dot{p}_{12}} = -\frac{\dot{p}_{12}}{\mu_{12}} \cdot \frac{\partial V_3}{\partial r_{12}} \quad (4.44a)$$

$$\uparrow$$

$$\frac{\partial E}{\partial r_{12}}$$

and

$$J_2 = -\frac{\partial E}{\partial \omega_{12}} \cdot \frac{\partial(E_{12} - B)}{\partial l_{12}} = -\left(\frac{l_{12}}{\mu_{12} r_{12}^2} - \frac{dB}{dl_{12}}\right) \frac{\partial V_3}{\partial \omega_{12}}. \quad (4.44b)$$

Substituting (4.44) into (2.26) and making the transformation (4.28) discussed in Section IV D, we obtain the expression

$$k_r^B(E_0) = fQ^{-1} \int_{S(B)} e^{-E/kT} \left(\frac{\dot{p}_{12}}{|\dot{p}_{12}|} \frac{\partial V_3}{\partial r_{12}} - \frac{\gamma_B \cos \beta_{12}}{r_{12}} \cdot \frac{\partial V_3}{\partial \alpha} \right) l_{12} \\ \times dp_3 dl_3 d\omega_3 dm_3 d\phi_3 d\beta_3 d\beta_{12} dl_{12} dr_{12} dr_3 d \cos \alpha, \quad (4.45)$$

where

$$\gamma_B(r_{12}, l_{12}, E_0) = \frac{(1 - 2\mu_{12} r_{12}^2 dB/dl_{12}^2)}{[2\mu_{12} r_{12}^2 (B - E_0 - V_{12})/l_{12}^2 - 1]^{\frac{1}{2}}}, \quad (4.46)$$

which is identical in form to (4.29).

Following Woznick,²³ we integrate (4.45) exactly over the first seven variables, obtaining

$$k_r^B(E_0) = f4 \left(\frac{2kT}{\mu_{12}}\right)^{\frac{1}{2}} \int_{r_B > 0} e^{\varepsilon - b - u} \Gamma\left(\frac{3}{2}, \frac{|b+u| - (b+u)}{2}\right) \\ \times F z^2 r_3^2 \frac{db}{dz} \left| \frac{\partial u}{\partial r_3} \right| dz dr_{12} dr_3 d \cos \alpha, \quad (4.47)$$

where $\varepsilon = E_0/kT$, $b = B/kT$, $u = V_3/kT$,

$$F(r_{12}, \alpha, r_3, z, E_0) = 4 \left(\eta \frac{\partial r_3}{\partial r_{12}} + \frac{\gamma_B \cos \eta}{r_{12}} \frac{\partial r_3}{\partial \alpha} \right), \quad \cong 0 \quad (4.48)$$

$$\gamma_B(r_{12}, z, E_0) = \left[1 - \left(\frac{r_{12}}{z}\right)^2 \right] \left[\left(\frac{r_{12}}{z}\right)^2 \frac{B - E_0 - V_{12}(r_{12})}{B - V_{12}(z)} - 1 \right]^{-\frac{1}{2}}, \quad (4.49)$$

and

$$\eta = \begin{cases} \sin^{-1} \left| \frac{r_{12}}{\gamma_B} \frac{\partial \alpha}{\partial r_{12}} \right| & : \quad \left| \frac{r_{12}}{\gamma_B} \frac{\partial \alpha}{\partial r_{12}} \right| \leq 1 \\ \frac{\pi}{2} & : \quad \left| \frac{r_{12}}{\gamma_B} \frac{\partial \alpha}{\partial r_{12}} \right| > 1 \end{cases} \quad (4.50)$$

Note that we have transformed from dl_{12} to dz by using (4.7).

We now assume, for simplicity, that $\partial u/\partial r_3$ has only one zero, corresponding to a single minimum in the interaction potential of depth $u_m(\alpha, r_{12})$ at a radius $r_{3m}(\alpha, r_{12})$. Under these conditions, the factor

$$e^{-b-u} \Gamma\left(\frac{3}{2}, \frac{|b+u| - (b+u)}{2}\right) \frac{db}{dz} \left| \frac{\partial u}{\partial r_3} \right|$$

in the integrand of (4.47) will have relatively strong maxima at the points (z_2, a_+) and (z_2, a_-) in the (z, r) plane defined by

$$\frac{\partial}{\partial z} \left[e^{-b} \Gamma\left(\frac{3}{2}, \frac{|b+u| - (b+u)}{2}\right) \frac{db}{dz} \right]_{z_2, a_{\pm}} = 0$$

and

$$\frac{\partial}{\partial r_3} \left[e^{-u} \Gamma\left(\frac{3}{2}, \frac{|b+u| - (b+u)}{2}\right) \left| \frac{\partial u}{\partial r_3} \right| \right]_{z_2, a_{\pm}} = 0, \quad (4.51)$$

where $a_+(\alpha, r_{12}) > r_{3m}(\alpha, r_{12}) > a_-(\alpha, r_{12})$. If we further assume that the remaining factor $Fz^2r_3^2$ varies relatively slowly, we may evaluate it at the points (z_2, a_+) and (z_2, a_-) and express (4.47) in the form

$$k_r^B(E_0) = f\pi z_2^2 \left(\frac{8kT}{\pi\mu_{12}}\right)^{\frac{1}{2}} [\Omega_+(E_0) + \Omega_-(E_0)] (1 - e^{-b_m(E_0)}) e^\epsilon, \quad (4.52)$$

where

$$\Omega_{\pm}(E_0) = \int_{r_{3m} > 0} F(r_{12}, \alpha, a_{\pm}, z_2, E_0) G_{\pm} a_{\pm}^2 d \cos \alpha dr_{12}, \quad (4.53)$$

$G_-(E_0) =$

$$\begin{aligned} & \frac{2}{\sqrt{\pi}} (1 - e^{-b_m(E_0)})^{-1} \int_{-u_m}^{\infty} du \int_0^{b_m(E_0)} db e^{-b-u} \Gamma\left(\frac{3}{2}, \frac{|b+u| - (b+u)}{2}\right) \\ & = e^{u_m} \left[\Gamma\left(\frac{7}{2}, u_m\right) \Gamma^{-1}\left(\frac{7}{2}\right) - e^{-b_m(E_0)} \right] / (1 - e^{-b_m(E_0)}), \quad (4.54a) \end{aligned}$$

and

$G_+(E_0) =$

$$\begin{aligned} & \frac{2}{\sqrt{\pi}} (1 - e^{-b_m(E_0)})^{-1} \int_{-u_m}^0 du \int_0^{b_m(E_0)} db e^{-b-u} \Gamma\left(\frac{3}{2}, \frac{|b+u| - (b+u)}{2}\right) \\ & = G_-(E_0) - 1. \quad (4.54b) \end{aligned}$$

In (4.54), $b_m(E_0)$ is the dimensionless height of the rotational barrier for which E_0 is just equal to the depth of the minimum in the effective potential curve, and we have tacitly assumed that

$b_m(E_0) \gtrsim u_m$. Note that $\Omega_{\pm}(E_0)$ is an effective interaction volume of molecular size.

Equation (4.52) is the general expression for the barrier rate constant. It is valid for all interaction potentials having at most a single minimum and sufficiently sharply cut-off to make the integrals convergent.

To proceed further we must now specify the nature of the interaction potential.

Dumbbell model. The only detailed calculations of the barrier rate constant (4.52) which have been made to date use the "dumbbell" model $V_3 = V_{13}(r_{13}) + V_{23}(r_{23})$ and are restricted to the case where the attractive minima in $V_{13}(r_{13})$ and $V_{23}(r_{23})$ are not deep compared to kT . As discussed in the preceding Section, the integral in (4.53) can then be expressed as a sum of contributions from the two ends of the "dumbbell"

$$\Omega_{\pm}(E_0) = 4\pi[z_2(E_0) - z_1(E_0)][a_{13\pm}^2(E_0) + a_{23\pm}^2(E_0)], \quad (4.55)$$

where $z_1(E_0)$ and $z_2(E_0)$ are, respectively, the inner and the outer turning point for a Morse oscillator with an energy $E_{12} = B - E_0$ and a rotational maximum at $z_2 \equiv z_2(0)$. $a_{1\pm}(E_0)$ and $a_{2\pm}(E_0)$ are effective radii given by

$$a_{j\pm}^2(E_0) = \mu_{12} m_j^{-1} a_{j3\pm}^2 \phi_{j\pm}(E_0) G_{j\pm}(E_0), \quad j = 1, 2 \quad (4.56)$$

for collisions with the two ends of the dumbbell. The factor $\phi_{j\pm}(E_0)$ in (4.56) is a slowly decreasing function of E_0 , which must be calculated numerically and for most molecules of interest is approximately 1/3. It is defined by the equation

$$\phi_{j\pm}(E_0) = \frac{1}{4} [z_2(E_0) - z_1(E_0)]^{-1} \int_{z_1}^{z_2} H(\theta_{j m_{\pm}}, \gamma_B) d r_{12},$$

where

$$H(\theta, \gamma_B) = \begin{cases} (1 + \gamma_B^2)^{\frac{1}{2}} \left(1 - \frac{\cos \theta}{|\cos \theta|} \right) + \frac{\cos \theta}{|\cos \theta|} \sin^2 \theta : \cot^2 \theta \geq \gamma_B^2 \\ \frac{2}{\pi} \left\{ (1 + \gamma_B^2)^{\frac{1}{2}} \tan^{-1} \frac{(\gamma_B^2 - \cot^2 \theta)^{\frac{1}{2}}}{(1 + \gamma_B^2)^{\frac{1}{2}} \cot \theta} + \right. \\ \left. \left[\sin^{-1} \frac{\cot \theta}{\gamma_B} - (\gamma_B^2 - \cot^2 \theta)^{\frac{1}{2}} \cot \theta \right] \sin^2 \theta \right\} : \cot^2 \theta \leq \gamma_B^2 \end{cases} \quad (4.58)$$

and θ_{jm} and γ_B are given by (4.37) and (4.49) with $z = z_2$. For $\theta \approx \pi/2$, $H \approx (1 + \gamma_B^2)^{1/2}$.

Combining (4.52), (4.55), and (4.56), we obtain the barrier rate constant in the form

$$k_r^B(E_0) = f\pi a^2(E_0)(4\pi z_2^2) [z_2(E_0) - z_1(E_0)] \left(\frac{8kT}{\pi\mu_{12}}\right)^{1/2} (1 - e^{-b_m(E_0)})e^\epsilon, \quad (4.59)$$

where

$$a^2(E_0) = \mu_{12} \left[\left(\frac{a_{13-}^2}{m_1} \phi_{1-G_{1-}} + \frac{a_{23-}^2}{m_2} \phi_{2-G_{2-}} \right) + \left(\frac{a_{13+}^2}{m_1} \phi_{1+G_{1+}} + \frac{a_{23+}^2}{m_2} \phi_{2+G_{2+}} \right) \right] \quad (4.60)$$

is the square of the effective collision radius.

The functions necessary to compute $k_r^B(E_0)$ for homonuclear molecules interacting with repulsive or only weakly attracting

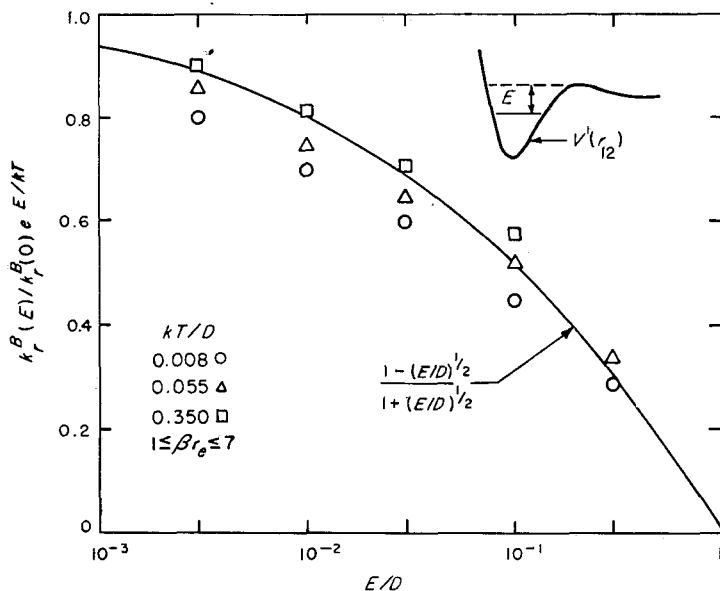


Fig. 4. Variation of the factor $k_r^B(E)$ defined by eqn. (4.59) with E/D for several values of kT/D . Note the dependence on kT/D is quite weak. The curve is the classical analogue of the square of the transition matrix elements for a Morse oscillator.

third bodies have been calculated by Woznick²³ and the writer⁴ and are summarized in Fig. 4 and 5. These functions may also be used for heteronuclear molecules whose force fields are only slightly asymmetric.

For most molecules $k_r^B(E_0)$ has a weak minimum a fraction of kT below the dissociation limit, and it is an excellent approximation to evaluate $k_r^B(E_0)$ at $E_0 = 0$. A comparison of $k_r^B(0)$ with

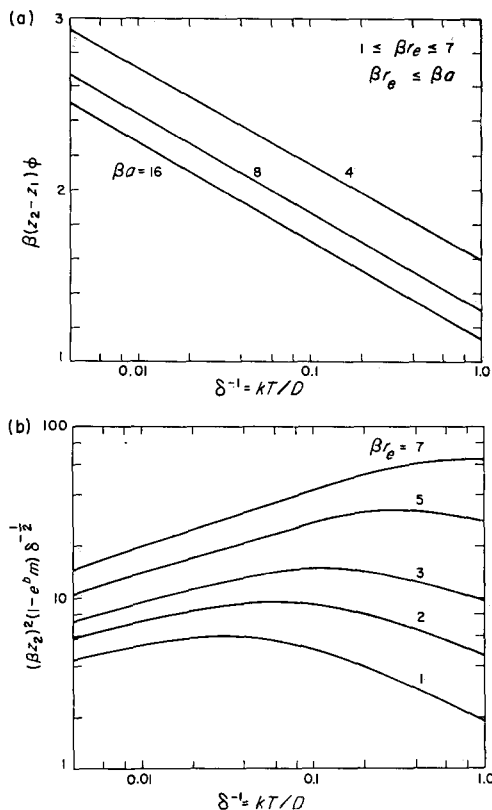


Fig. 5. Parametric curves for computing the barrier rate constant $k_r^B(0)$ for the surface tangent to the top of the rotational barrier.

the rate constants calculated previously is shown in Fig. 3. For $\mu_{12} \sim \mu_3$ it is less than either the Wigner or available energy rate constants and of the same magnitude as the three-body collision

rate constant. It is much less arbitrary than the three-body collision rate constant, however, since the effective collision volume is explicitly related to the interaction potential. This permits one to compare attractive and repulsive potentials and to investigate the relative contributions due to rotational and vibrational transitions. For example, one can see immediately from (4.54) that potentials having an attractive minimum will give a strong negative temperature coefficient for $kT \lesssim V_{3m}$.

The barrier rate constants agree quite well with flash-photolysis experiments on recombination in various gases near room temperature but overestimate the dissociation rates observed in shock tubes at high temperatures by a factor of from 3 to 10. This is, of course, not too surprising since the barrier rate is only rigorously an upper limit. What is somewhat surprising (and disappointing) is that more detailed investigations have shown that this effect can not be attributed either to recrossing corrections²⁴ or non-equilibrium²⁵ near the dissociation limit. The writer has therefore been led to the conclusion that it may be due to a failure of the "dumbbell model" which undoubtedly overestimates the angular asymmetry in the interaction potential and, therefore, overestimates the contribution from rotational transitions. Since rotational transitions dominate at high temperatures,⁴ this could explain the effect. Failure of the "dumbbell model" would, of course, occur if $V_3 \neq V_{13}(r_{13}) + V_{23}(r_{23})$. This is quite likely, and calculations of the barrier rate constant with more realistic potentials should be made. In particular, the case of strongly attracting third bodies is badly in need of investigation.

V. CORRECTIONS AND EXTENSIONS

In addition to providing a systematic method for estimating rate constants, the variational theory is also a convenient starting point for the detailed numerical investigation of collision processes by Monte Carlo methods. The technique involves the random sampling of trajectories crossing the trial surface, followed by numerical integration of the equations of motion both forward and backward in time to determine the complete history of a collision. By sampling with a weight proportional to the local flow rate $\rho(\mathbf{v} \cdot \mathbf{n})$ across the surface, one obtains a statistical

distribution of trajectories which reflects their *a priori* contribution to the reaction rate. Further, by choosing surfaces which pass through the reaction zone and integrating out, one can terminate the integrations as soon as the interactions become negligible. Both these factors contribute to the overall efficiency of the calculations,

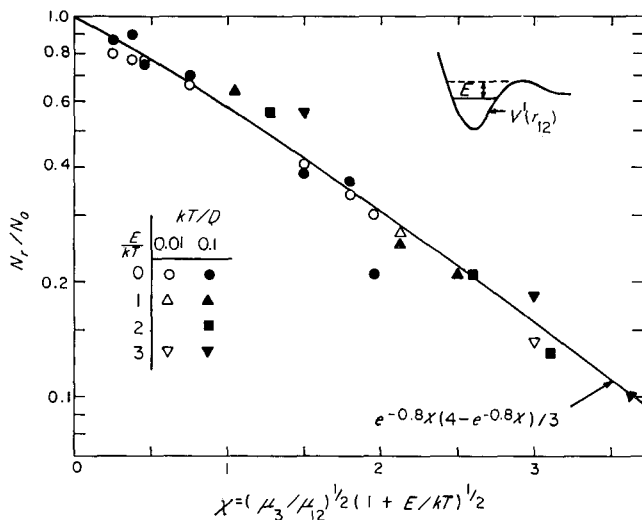


Fig. 6. Fraction of trajectories corresponding to a reaction as a function of a parameter χ for temperature $kT/D = 0.01$ and 0.1 and surface $E/kT = 0, 1, 2,$ and 3 . The points represent calculations made for $I_2 + He, I_2 + Ar, O_2 + Ar, O_2 + Xe,$ and $H_2 + Ar$ in the order of increasing μ_3/μ_{12} . The statistical accuracy of the data varies from 5 per cent to 10 per cent. Individual points may be identified by calculating χ from μ_3/μ_{12} and E/kT . The correlation parameter χ was arrived at empirically but is very nearly the adiabaticity parameter $\omega\tau$ for the collisions. The curve has the form expected for a linear harmonic oscillator subjected to an impulse of duration τ .

which is typically very much greater than that obtained when one samples on surfaces outside the reaction zone.

Monte Carlo methods were used by the writer²⁴ to investigate the recrossing correction for the trial surface at the top of the rotational barrier and extended by Woznick²⁶ to surfaces below the barrier. Calculations have been made for the systems $H_2 + Ar, O_2 + Xe, O_2 + Ar, I_2 + Ar,$ and $I_2 + He$ at

temperatures, $kT/D = 0.01$ and 0.1 , and for surfaces $E_0/kT = 0, 1, 2,$ and 3 . The recrossing corrections are summarized in Fig. 6 which shows the fraction of reacting trajectories as a function of a parameter χ which is closely related to the product of the angular frequency ω of the oscillator and the collision time τ . It can be seen that this parameter correlates the results quite well and that the corrections are essentially temperature-independent. This was the basis of our statement in the preceding section that recrossing could not account for the negative temperature coefficient observed in most recombination reactions.

One of the most important facts to emerge from the calculations was that the average energy transfer in molecules undergoing dissociation or recombination is less than $\frac{1}{2}kT$. This was a surprise to the writer who had previously thought that large energy transfer would be favored owing to the high velocity acquired by the attracting atoms as they approach one another. The reason why this is not the case is that most of the collisions with the third body occur at a time when the atoms are only weakly interacting because of the larger volume of configuration space available for distant collisions. An important corollary is that detailed conclusions about atomic collisions based on square well or truncated harmonic oscillator potentials can be grossly incorrect since these potentials have no tails where weak interactions can occur. This point is made to emphasize the need for using realistic potentials in calculations of atomic collision processes.

There is, of course, a wealth of other information about atomic collision in the results, but a discussion of this is outside the scope of this paper. The general conclusion which the writer would like to draw is, however, that the variational theory supplemented by Monte Carlo trajectory calculations is a powerful tool for investigating atomic collision processes. It is also felt that the most important weakness in the present calculations is due to the approximate potentials used, and it is hoped that further investigations in this area will lead to significant improvements.

VI. ACKNOWLEDGMENTS

The writer acknowledges the encouragement and support of A. R. Kantrowitz, Director of the Avco-Everett Research Laboratory,

where much of this work was performed. This review is based in part on a lecture presented at the Summer Institute on Chemical Physics held at UCSD, La Jolla, during August 1965. Its preparation was supported in part by the Advanced Research Projects Agency (Ballistic Missile Defense Office) and technically administered by the Fluid Dynamics Branch of the U.S. Office of Naval Research under Contract Nonr-1841(93).

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