Dynamics of
Molecular Collisions

Part B

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Statistical Approximations in Collision Theory

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1. Introduction

This chapter is an introduction to statistical approximation in the theory of reactive collisions. The theme of the chapter is the transition state,* and the statistics in statistical theory is in essence just the counting of the various ways a system can pass through a transition state.

The aim of statistical theory is to bypass collision dynamics en route to rate constants and cross sections. To bypass, but not to ignore: One of the attractions of statistical theory is that at heart it is founded in dynamics, not in the trivial sense that every scheme of approximation in collision theory is ultimately founded in dynamics but in the sense that statistics and dynamics are inseparable and complement each other at the base of the theory. To define a transition state properly is to solve a dynamical problem: A transition state is a condition of dynamical instability, motion to one side of the state differing qualitatively in character from motion to the other side.

We shall discuss both the transition state theory of direct reactions (one transition state, separating reactants from products) and the transition state theory of complex reactions (two transition states, one separating reactants from complex and another separating complex from products). Nothing here is new,† and much is very old. Nevertheless, the ideas are definitely part of the

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*Many writers prefer the term *activated complex*. It is a matter of personal taste.
†With the possible exception of some observations on nuclear symmetry along reaction paths that the author has not been able to find in the literature.

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core of modern theoretical chemistry and are discussed in detail in many recent texts, such as the excellent books by Bunker,[1] Johnston,[2] Laidler,[3] Levine and Bernstein,[4] and Nikitin.[5] The reader should consult these works for other points of view, for information on the history of transition state theory, and for additional bibliography.

A short discussion of a long topic must of necessity be limited in scope, limited by the interests and even more by the competence of the writer. This chapter is seriously deficient in at least two respects. First, we shall not present any numerical calculations. Numerical work is, of course, essential to assess the validity of an approximation and to suggest modifications in the theory. Classical transition state theory has reached a definitive and natural form unlikely to change, and the same is true of the quantum theory of "loose" transition states. Quantum theory of "tight" transition states is another matter, and as accurate quantum calculations in three dimensions become available we may look forward to numerical studies of the sort mentioned in Section 3.1 for guidance in setting the final form of the theory. Second, we shall not discuss the random phase approximations or average S-matrix methods applicable both to reactive and nonreactive scattering problems. Here there are excellent presentations by Levine[6] and others[7,8] that the reader may consult with profit.

2. Classical Transition State Theory of Direct Reactions

2.1. Once Over Lightly

Consider a bimolecular reaction in the gas phase,

$$A+B \underset{k_b}{\overset{k_f}{\rightleftharpoons}} C+D \tag{1}$$

and suppose that the reaction proceeds through an intermediate, designated by *:

$$A+B \rightleftharpoons * \rightleftharpoons C+D \tag{2}$$

At chemical equilibrium the concentrations of A, B, C, D, and * are fixed, and if the gas is sufficiently dilute these concentrations may be expressed in terms of partition functions of the individual species; in particular,

$$\frac{[*]}{[A][B]} = \frac{Q^*}{Q_A Q_B} \tag{3}$$

where [ ] indicates number per unit volume and Q_A, Q_B, and Q^* are the partition functions per unit volume of A, B, and *. That is,

$$Q_A = h^{-3N_A} \int d\Gamma_A \exp(-H_A/kT) \tag{4}$$

where N_A is the number of atoms in A, H_A is the Hamiltonian of isolated molecule A, and the integration in the phase space of A is restricted to points Γ_A where the internal energy of A lies below the first dissociation limit and the center of mass of A lies within a spatial region of unit volume. [The factor h^{-3N_A} is customarily included in the classical partition function to give an approximately correct counting of quantum states; for the same reason we should have appropriate factorials in the denominator if the atoms of A are not all distinguishable (see Section 2.4.)]

The partition function Q_B is similarly defined; Q^* is a little more difficult to define. The Hamiltonian appropriate to the intermediate $*$ is the full Hamiltonian of the system of $N = N_A + N_B = N_C + N_D$ atoms; the intermediate is not stable but rather a region of phase space through which reactants have to pass to become products, and Q^* is the partition function associated with this region, again per unit volume swept out by the center of mass of the entire N-atom system.

In this section we have in mind direct reactions with a more or less abrupt passage from reactant to product. We suppose that the intermediate is a thin region of phase space, of narrow width δ along a "reaction coordinate" q measuring progress from reactants to products; we suppose further that in the vicinity of the intermediate the full Hamiltonian takes the form

$$H = H^{\ddagger} + p^2/2m^* \tag{5}$$

where p is the momentum conjugate to q, m^* is the associated mass, and $H^{\ddagger}$ is independent of p and q. Then

$$Q^* = Q^{\ddagger}(\delta/h)(2\pi m^* kT)^{1/2} \tag{6}$$

where $Q^{\ddagger}$ is the integral of $\exp(-H^{\ddagger}/kT)$ over the remaining $3N-1$ coordinates and $3N-1$ momentum perpendicular to p and q (subject again to the restriction that the center of mass of the system be confined to a unit volume), divided by h^{3N-1}.

Chemical equilibrium is dynamic, and a given intermediate has a rather brief life. In a time dt all intermediates with velocity p/m^* pointing in the product direction along q, and lying within $p\,dt/m^*$ of the product "edge," will disappear to become product. The number of complexes that disappear in this manner, per unit volume, is the concentration of complexes times the probability that a given complex suffers this fate, that is,

$$\frac{[*]\int_0^{\infty} dp(p\,dt/m^*)\exp(-p^2/2m^*kT)}{\delta\int_{-\infty}^{+\infty} dp\,\exp(-p^2/2m^*kT)} = \frac{[*]kT\,dt}{\delta(2\pi m^*kT)^{1/2}} \tag{7}$$

We identify the rate of disappearance of intermediate over the product edge as the forward rate of the reaction, $k_f[A][B]$; comparison with Eqs. (3) and (6)

gives

$$k_f = \frac{kT}{h} \frac{Q^{\ddagger}}{Q_A Q_B} \tag{8}$$

Similarly, the rate of disappearance of intermediate over the reactant edge is the backward rate $k_b[C][D]$, and we find

$$k_b = \frac{kT}{h} \frac{Q^{\ddagger}}{Q_C Q_D} \tag{9}$$

The ratio k_f/k_b is of course just the statistical expression for the equilibrium constant, as it should be.

These formulas are purely classical. The h that appears in Eqs. (8) and (9) is Planck's constant, the quantum of action, but it is not really there: $Q^{\ddagger}$ contains one less h in its denominator than the products $Q_A Q_B$ or $Q_C Q_D$.

This is classical transition state theory, and it is remarkably simple, but there are questions and a paradox. The paradox: Kinetics is supposed to be an exercise in dynamics, but all the dynamics has disappeared—literally, over the edge in the argument above—and we are left only with the task of calculating partition functions. The questions: First, how to define the "transition state" ‡? And second, what relation do the rates calculated above—which are rates for a macroscopically unobservable process (passage through a surface in phase space) occurring in a macroscopically static situation (complete chemical equilibrium)—bear to the thermal reaction rates measured in the laboratory or calculated by the methods of molecular dynamics?

It is most helpful to discuss complicated questions with the aid of simple models, and in the next two sections we shall look at transition state theory as it applies to one- and two-dimensional models of chemical reactions.

2.2. Dynamical Foundations: A One-Dimensional Model

The classical problem of barrier passage in one dimension is trivial: Particles with energy above the top of the barrier can get across, particles with energy below the top of the barrier are reflected, and particles with energy just equal to the barrier height spend their life trying to reach the top. The problem can be used as a crude model for chemical kinetics by imagining a gas of noninteracting particles moving in one dimension in the presence of the barrier, particles to the left labeled reactant and particles to the right labeled product (Fig. 1). We assume an initial equilibrium distribution of reactants, of density one particle per unit length on the potential-free region to the left of the barrier, and no product. We calculate the rate of formation of product assuming that the reactant and product regions extend to infinity—no walls— so that once across the barrier a particle continues to move to the right. In this

Fig. 1. One-dimensional model for transition state theory of direct reactions.
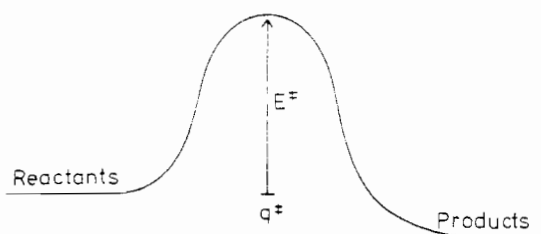
model there is no back reaction, equilibrium is never reached, and after a period of confusion in which the rate of product formation depends on details of the initial distribution right around the barrier, the rate of product formation is constant and equal to the number of particles per unit time that cross a fixed point q to the left of the barrier with energy sufficient to cross the barrier. Because

$$\rho(p)\,dp = \exp(-p^2/2mkT)\,dp/(2\pi mkT)^{1/2} \qquad (10)$$

is the probability that a reactant particle has momentum between p and $p+dp$, and because all particles with positive momentum p and lying in the interval $(q-p/m, q)$ will cross q in a unit of time, the rate of product formation is

$$k = \int_{(2mE^{\ddagger})^{1/2}}^{\infty} \frac{p}{m}\rho(p)\,dp = kT\frac{\exp(-E^{\ddagger}/kT)}{(2\pi mkT)^{1/2}} \qquad (11)$$

In this model k is in fact the forward rate constant for reaction, because the density of reactants is unity; we have dropped the subscript f on k and hope the reader will not confuse rate constants k and Boltzmann's constant k.

Now for transition state theory. Years of looking in textbooks at diagrams similar to Fig. 1 lead us automatically to choose the point $q^{\ddagger}$—the location of the barrier maximum—as the transition state. The Hamiltonian is $H = p^2/2m + V(q)$. At $q^{\ddagger}$, $H = p^2/2m + E^{\ddagger}$, and because the partition function of reactants per unit "volume" is $(2\pi mkT)^{1/2}/h$, the transition state rate constant [Eq. (8)] is

$$k_{\text{TS}} = \frac{kT}{h}\frac{\exp(-E^{\ddagger}/kT)}{(2\pi mkT)^{1/2}/h} = k \qquad (12)$$

For this model problem transition state theory is exact.

We can make the entire calculation look slightly less juvenile by introducing an obscure notation. Consider the phase space of a single one-dimensional particle and define on it a function $\chi_r(p, q)$, the characteristic function of reactive phase points, by $\chi_r(p, q) = 1$ if (p, q) lies on a reactive trajectory, and $\chi_r(p, q) = 0$ otherwise. That is, $\chi_r(p, q) = 1$ if in the indefinite past a particle following the classical trajectory through (p, q) lies in the reactant region, and in the indefinite future in the product region. For our model problem $\chi_r(p, q) = 1$ if $p > 0$ and $H(p, q) > E^{\ddagger}$, and 0 otherwise. The function

$\chi_r(p, q) \exp[-H(p, q)/kT]$ is a phase space density (i.e., a nonnegative function of phase point), identical to the equilibrium density $\exp(-H/kT)$ on reactive phase points and zero elsewhere. The equilibrium rate constant k, Eq. (11), is proportional to the classical flux of this density through the surface in phase space defined by the equation $q =$ constant, where q is any point in the reactant region:

$$k = (2\pi mkT)^{-1/2} \int dp(p/m)\chi_r(p, q) \exp[-H(p, q)/kT] \qquad (13)$$

Equation (13) is just Eq. (11) in disguise.

   Two remarks about the phase space density $\chi_r(p, q) \exp[-H(p, q)/kT]$ are essential to an understanding of equilibrium rate theory and the transition state approximation to it. First, calculating $\chi_r(p, q)$ is a *dynamical* problem: we must follow the classical trajectory through (p, q) and check whether or not we have reactant in the indefinite past and product in the indefinite future. For the present model, of course, this is a trivial dynamical problem, but dynamical nonetheless. Second, $\chi_r(p, q)$ is constant along a given classical trajectory— either zero or one at all points on the trajectory—and therefore the density $\chi_r(p, q) \exp[-H(p, q)/kT]$ is an "invariant density" in phase space, constant along every trajectory (the numerical value of the Hamiltonian of course does not change along a given trajectory). This implies (remember Liouville's equation) that the classical flux associated with this phase space density, through any surface in phase space, is a constant provided only that all reactive trajectories pass through the surface.

   For our model problem all reactive trajectories pass every point q on the axis, so that flux integral of Eq. (13) must be completely independent of q, a fact that the reader can verify by direct computation. In particular we may just as well evaluate the correct equilibrium rate constant at the transition state $q\ddagger$:

$$k = (2\pi mkT)^{-1/2} \int dp(p/m)\chi_r(p, q^\ddagger) \exp[-H(p, q^\ddagger)/kT] \qquad (14)$$

Transition state theory calculates the rate of reaction as the rate at which phase points leave the transition state *to the product side*. This amounts to replacing $\chi_r(p, q^\ddagger)$ by $\chi_+(p, q^\ddagger)$, the characteristic function of phase points with positive momentum:

$$\chi_+(p, q) = \begin{cases} 1, & p > 0 \\ 0, & \text{otherwise} \end{cases} \qquad (15a)$$

$$k_{TS} = (2\pi mkT)^{-1/2} \int dp(p/m)\chi_+(p, q^\ddagger) \exp[-H(p, q^\ddagger)/kT] \qquad (15b)$$

   Dynamics disappears in the replacement $\chi_r \rightarrow \chi_+$. To evaluate χ_r we must examine the entire trajectory through (p, q); to evaluate χ_+ we need only look at the sign of the momentum at (p, q). Transition state theory is exact for this model problem because, *at $q^\ddagger$, $\chi_r = \chi_+$ for all p*.

What governs the choice of transition state? In this model problem *any q* is, in a sense, a point of transition between reactant and product, because every reactive trajectory must at some time cross any *q*. At any *q* but $q^\ddagger$, however, $\chi_+(p, q)$ does *not* equal $\chi_r(p, q)$ for all *p*, and then the transition state rate constant cannot—even by accident—equal the correct equilibrium rate constant: It is not only sufficient but also necessary that $\chi_+(p, q) = \chi_r(p, q)$ at the transition state if transition state theory is to be exact. The reason, in this one-dimensional model, is simple: χ_r and χ_+ both vanish if the sign of the momentum *p* is negative, whereas if *p* is positive, χ_+ by definition equals 1 whereas χ_r may be zero. Transition state theory, then, gives a rate constant that is never less than the correct equilibrium rate constant, and the best choice of transition state is that state that minimizes the transition state rate constant, i.e., the state that minimizes the partition function $Q^\ddagger$. In this one-dimensional model problem the criterion is purely energetic. There is only one coordinate, which is naturally the reaction coordinate, and we should choose the transition state at the point of maximum potential energy along that coordinate. In more than one dimension entropy is a consideration as well, and the best choice of transition state is not automatically the region of highest energy along the reaction coordinate (see Section 2.3).

The correct transition state $q^\ddagger$ is a point of instability for dynamics in one dimension. There is a phase point that remains on the transition state for all time, the point with $p = 0$. A little shove to the right and the point inevitably becomes product; a little shove to the left and the point inevitably becomes reactant. At the transition state we have a qualitative change, at $p = 0$, in the character of the classical motion.

It is instructive to compare the discussion of this section with the derivation of transition state theory given in Section 2.1. In that derivation we calculated rates that are macroscopically unobservable, rates of reaction forward and back at complete chemical equilibrium. In this section we posed a problem that in its initial conditions was a step closer to experimental gas kinetics: an initial equilibrium distribution of reactants and, initially, no products. Shortly—within the time it takes reactants to climb the potential barrier—a steady state distribution is reached in the neighborhood of the transition state, and we have *partial* equilibrium in the interaction region. At $q^\ddagger$ itself we have an equilibrium distribution in the single-particle phase space *insofar as the positive momenta are concerned*. At other phase points in the neighborhood of the transition state the distribution is the equilibrium distribution if the point can be reached classically by a particle that in the indefinite past was reactant, and zero otherwise.

In general, if isolated reactants are in thermal equilibrium, distributed à la Maxwell–Boltzmann over their possible states, then rapidly—in roughly a single collision—dynamics ensures a partial equilibrium between isolated reactants and reactants in collision: States of interaction that evolve from

isolated reactant states are populated according to the Maxwell–Boltzmann distribution. This is an important point,* occasionally missed in discussions of the so-called "equilibrium assumption" in transition state theory.

The equilibrium rate constant, defined by Eq. (13) in terms of the *reactive* phase space density $\chi_r \exp(-H/kT)$, may be expressed as well in terms of the partial equilibrium density of interacting states described above, and we shall do so in the next paragraph because the quantum analogue of the expression is central to recent discussions of quantum transition state theory (see Section 3.2). First, however, we emphasize that rapid equilibrium between isolated reactants and colliding reactants does not in itself guarantee that the equilibrium rate constant is what one measures in a gas–kinetic experiment. A reacting gas mixture is under no obligation to maintain the reactants in thermal equilibrium.

Describing the evolution of a reacting mixture is a difficult statistical mechanical problem that has attracted considerable attention over the years, particularly in the last decade and a half.[10] We shall make only two obvious comments. First, if one enforces thermal equilibrium on the reactants at all times, then one can be sure that the observed rate is the equilibrium rate. In the one-dimensional model of this section we enforced thermal equilibrium on reactants approaching the barrier by providing an infinite sink of thermally equilibrated reactant to the left—remember, no walls. This is a ruse not available in real life, but running the reaction at great dilution in nonreactive "buffer" gas accomplishes the same trick, by ensuring that the rate of equilibration among states of the isolated reactants—by collision with the "buffer"—is much greater than the rate of reaction. Second, we expect nonequilibrium effects to lower the instantaneous rate of reaction below that given by equilibrium theory, for the population of reactant molecules in highly reactive states will be depleted by reaction faster than the population of less reactive states, so the bias in the instantaneous distribution of reactants—relative to an equilibrium distribution—should lie toward the sluggards.

Consider now the partial equilibrium established in phase space by an equilibrium distribution of isolated reactants. The phase points populated are those lying on trajectories that in the indefinite past were reactant. Let $\chi(p, q)$ be the characteristic function of these phase points. For the one-dimensional model of Fig. 1 we have $\chi(p, q) = 1$ if (1) $H(p, q) > E^{\ddagger}$ and $p > 0$; or (2) $H(p, q) = E^{\ddagger}$, $p > 0$, and $q < q^{\ddagger}$; or (3) $H(p, q) < E^{\ddagger}$ and $q < q^{\ddagger}$. Otherwise, $\chi(p, q) = 0$.

We can write the equilibrium rate constant equally well in terms of the characteristic function χ:

$$k = (2\pi mkT)^{-1/2} \int dp(p/m)\chi_r(p, q) \exp[-H(p, q)/kT]$$

$$= (2\pi mkT)^{-1/2} \int dp(p/m)\chi(p, q) \exp[-H(p, q)/kT]$$

(16)

*A forceful discussion of this point was given recently by Anderson.[9]

an equality that may be verified by direct calculation. The reason for it is that χ combines χ_r, the characteristic function of reactive trajectories, with χ_{nr}, the characteristic function of nonreactive trajectories (trajectories that start in the indefinite past as reactant but never make it to product). $\chi_{nr} \exp(-H/kT)$ is an invariant phase space density with no flux through any phase space surface in the product region—because χ_{nr} is zero in the product region—and therefore no flux through *any* surface separating reactants from products. The nonreactive trajectories are reflected from the barrier (with the exception of the single trajectory at $H = E^{\ddagger}$), and positive flux passing through q on the way in is cancelled by negative flux through q on the way out.

In classical theory there is no good reason to complicate matters by using χ rather than χ_r. In quantum theory, however, χ has an analogue (a projection operator onto states that in the indefinite past were reactant), but χ_r does not.

2.3. Dynamical Foundations: A Two-Dimensional Model

As a two-dimensional model for chemical kinetics we shall consider particles of unit mass moving on the plane under the influence of a potential $V(q_1, q_2)$, particles in one region of the plane labeled reactant and particles in another region labeled product. Classical mechanics in two dimensions is a good deal more complicated than in one, and with this model we even make some small contact with reality: If the exchange reaction $A + BC \rightarrow AB + C$ is forced to take place with all three atoms at all times collinear, the potential energy V of the three-atom system is a function of two variables (for instance, the AB and BC distances d_{AB} and d_{BC}), and in the center of mass frame and after a suitable linear change of coordinates from (d_{AB}, d_{BC}) to (q_1, q_2) the motion of the system is that of a unit mass in the potential V expressed as a function of (q_1, q_2). Details of the coordinate transformation may be found in the standard texts, and considerable discussion of collinear atom–diatom collisions is given in Chapter 2 of Part B. Here we shall concentrate on the dynamical problem of motion of a unit mass on the plane and on the use and validity of transition state theory for reaction rates in such a model.

The potential energy surface $V(\mathbf{q})$ is conveniently represented by a map of the equipotentials $V = $ constant. For a reaction with activation energy the map might look like Fig. 2, where we also indicate some lines of constant d_{AB} and d_{BC} to remind the reader of the collinear atom–diatom problem lurking in the background. In the lower right we have reactant (d_{AB} large, d_{BC} small); in the upper left we have product (d_{AB} small, d_{BC} large); out in "center field" we have the region of three free atoms (d_{AB} and d_{BC} large). At any point the force on a unit mass is $-\boldsymbol{\nabla} V$, where $\boldsymbol{\nabla}$ is the two-dimensional gradient. The force is perpendicular to the equipotential through that point and in the direction of decreasing potential.
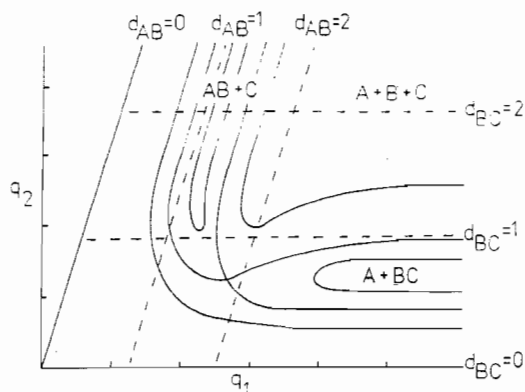
Fig. 2. Two-dimensional model for transition state theory of direct reactions. Map of the equipotentials.

Note in Fig. 2 that two equipotentials cross in the region of interaction (d_{AB} and d_{BC} small). The point of crossing is the so-called saddle point of the surface; $\nabla V = 0$ there, and in the immediate neighborhood the potential is parabolic downward in one direction through the saddle point and parabolic upward in the perpendicular direction through the saddle point. For a potential shaped as in Fig. 2 the potential energy at the saddle point is the classical threshold for reaction: A reactant particle must have total energy at least this great to have a chance of becoming product, for otherwise the motion of the particle is restricted to the U-shaped portion of the reactant region defined by the appropriate equipotential $V = E$.

We are interested in reactive trajectories for the process $A + BC \rightarrow AB + C$, that is, trajectories on which in the indefinite past d_{BC} is bounded but d_{AB} is not, whereas in the indefinite future d_{AB} is bounded but d_{BC} is not. Figure 3 illustrates some of the possibilities for classical motion in two dimensions: a reactive trajectory giving vibrationally excited product, a nonreactive trajectory leading from reactant back to reactant with vibrational deexcitation, and a nonreactive trajectory along which a speedy A smashes into BC and dissociates it. Nonreactive trajectories do not contribute to the reaction rate. We exclude them by defining the characteristic function of reactive trajectories
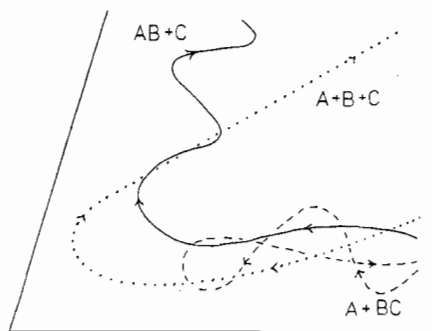

Fig. 3. Classical trajectories in the plane: reactive (——), nonreactive (– –), and nonreactive dissociative (· · ·).

$\chi_r(\mathbf{p}, \mathbf{q})$: $\chi_r = 1$ if $(\mathbf{p}, \mathbf{q})$ lies on a reactive trajectory, and zero otherwise. As in one dimension, we need only χ_r to calculate the reaction rate, and as in one dimension, evaluating χ_r at any point $(\mathbf{p}, \mathbf{q})$ is a dynamical problem that involves looking at the entire history of the trajectory through $(\mathbf{p}, \mathbf{q})$.

We assume an initial equilibrium distribution of reactants and no products. The phase space density $\chi_r(\mathbf{p}, \mathbf{q}) \exp[-H(\mathbf{p}, \mathbf{q})/kT]$ is invariant, and in the steady state the rate of product formation will be proportional to the flux of this density across any surface in phase space separating reactants from products, that is, any surface through which every reactive trajectory must pass. We can construct such a surface in a particularly simple manner by laying a curve on the plane in such a way that the asymptotic reactant region (d_{BC} bounded, $d_{AB} \to \infty$) lies to one side of the curve and the asymptotic product region (d_{AB} bounded, $d_{BC} \to \infty$) to the other side (see Fig. 4). Any such curve will do; parametrize it by arc length s, so that $\mathbf{q}_s$ is the point on the curve a distance s along from the start, and let $\mathbf{n}_s$ be the unit normal to the curve at $\mathbf{q}_s$ pointing to the product side (Fig. 4). The surface in phase space that we have in mind is the three-dimensional set $\{\mathbf{q}_s, \text{ all } \mathbf{p}\}$, and the thermal rate constant is proportional to the thermal flux of reactive trajectories through this surface,

$$k = Q^{-1} \int d\mathbf{p} \, ds (\mathbf{p} \cdot \mathbf{n}_s) \chi_r(\mathbf{p}, \mathbf{q}_s) \exp[-H(\mathbf{p}, \mathbf{q}_s)/kT] \qquad (17)$$

where Q is the partition function of isolated reactants per unit distance along the q_1 axis, with Planck's constant omitted for simplicity of notation.

The elementary interpretation of Eq. (17) is that all reactive particles with momentum $\mathbf{p}$ and lying in the skewed rectangle with corners at $\mathbf{q}_s$, $\mathbf{q}_{s+ds}$, $\mathbf{q}_s - \mathbf{p} \, dt$, and $\mathbf{q}_{s+ds} - \mathbf{p} \, dt$ will cross the curve in time dt. The area of this skewed rectangle is $ds|\mathbf{p} \cdot \mathbf{n}_s| \, dt$. If $\mathbf{p} \cdot \mathbf{n}_s$ is positive, these particles add to the instantaneous population on the product side of the curve; if $\mathbf{p} \cdot \mathbf{n}_s$ is negative, these particles subtract from the instantaneous product population. On balance, of course, we have net addition to the product region, and in fact if we draw the curve $\mathbf{q}_s$ far out in either the reactant or product region, all reactive trajectories will cross with $\mathbf{p} \cdot \mathbf{n} > 0$. If $\mathbf{q}_s$ lies in the region of interaction, however, we may find reactive trajectories that in the course of their meandering through the
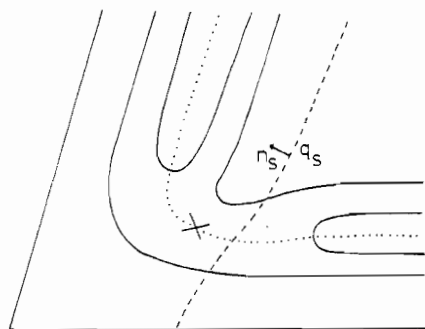

Fig. 4. Equipotentials (——), transition state curve $\mathbf{q}_s$ (– –), unit normal $\mathbf{n}_s$ in the product direction, and reaction path ($\cdots$).

plane cross the curve in the "wrong" direction. These crossings must still be counted, with appropriate sign, in the flux integral.

Transition state theory sets the rate of reaction equal to the total rate at which particles, in complete equilibrium, cross the transition state to the product side. Here the transition state is defined by the entire curve $\mathbf{q}_s$, and

$$k_{TS} = Q^{-1} \int d\mathbf{p} \, ds (\mathbf{p} \cdot \mathbf{n}_s) \chi_+(\mathbf{p}, \mathbf{q}_s, \mathbf{n}_s) \exp[-H(\mathbf{p}, \mathbf{q}_s)/kT] \qquad (18)$$

where

$$\chi_+(\mathbf{p}, \mathbf{q}, \mathbf{n}) = \begin{cases} 1, & \mathbf{p} \cdot \mathbf{n} > 0 \\ 0, & \text{otherwise} \end{cases} \qquad (19)$$

Dynamics disappears in the replacement $\chi_r \to \chi_+$: To evaluate χ_+ we need merely examine the sign of $\mathbf{p} \cdot \mathbf{n}$ at the point $(\mathbf{p}, \mathbf{q})$.

The momentum integral in Eq. (18) can be done immediately. Because

$$H(\mathbf{p}, \mathbf{q}_s) = \mathbf{p}^2/2 + V(\mathbf{q}_s) = (\mathbf{p} \cdot \mathbf{n}_s)^2/2 + p_s^2/2 + V(\mathbf{q}_s) \qquad (20)$$

where p_s is the projection of $\mathbf{p}$ along the curve $\mathbf{q}_s$ at s, we find

$$k_{TS} = kTQ^{-1} \int dp_s \, ds \exp\{-[p_s^2/2 + V(\mathbf{q}_s)]/kT\} \qquad (21)$$

and what we have to calculate is a "reduced partition function" associated with the transition state curve $\mathbf{q}_s$.

A caution: Unless the force between any pair of atoms vanishes identically beyond some finite distance, it is conceivable that a reactive trajectory might extend arbitrarily far into the region of three nearly free atoms. Such trajectories contribute negligibly to the true thermal rate constant, because exchange reactions go at energies well below the energy of dissociation: A new bond is formed as the old is broken. Still, these trajectories must in principle be counted. To be certain that all reactive trajectories pass through the curve $\mathbf{q}_s$ we must extend this curve indefinitely far into the region of three free atoms. There the potential is bounded and the integrals (18) and (21) diverge.

It is useful, therefore, to define "microcanonical" rate constants $k(E)$ and "microcanonical" transition state theory $k_{TS}(E)$ by

$$Qk = \int dE \, k(E) \exp(-E/kT) \qquad (22a)$$

$$k(E) = \int d\mathbf{p} \, ds (\mathbf{p} \cdot \mathbf{n}_s) \chi_r(\mathbf{p}, \mathbf{q}_s) \delta(E - H(\mathbf{p}, \mathbf{q}_s)) \qquad (22b)$$

and

$$k_{TS}(E) = \int d\mathbf{p} \, ds (\mathbf{p} \cdot \mathbf{n}_s) \chi_+(\mathbf{p}, \mathbf{q}_s, \mathbf{n}_s) \delta(E - H(\mathbf{p}, \mathbf{q}_s)) \qquad (23)$$

To calculate $k(E)$ we need only reactive trajectories with total energy E, that is, we need $\chi_r(\mathbf{p}, \mathbf{q}_s)$ only for momenta that satisfy $\mathbf{p}^2/2 + V(\mathbf{q}_s) = E$. To calculate $k_{TS}(E)$ we need only the portion of the curve $\mathbf{q}_s$ lying in the region $V(\mathbf{q}) \le E$;

First do the dp_s integral and then goes from 0 to $\sqrt{2[E-V-q_s]}$ because E is fixed. $dp_M = d(p \cdot n_s)$ integral

Statistical Approximations in Collision Theory   281

explicitly, on performing the momentum integral we find

$$k_{TS}(E) = 2 \int ds \{2[E - V(\mathbf{q}_s)]\}^{1/2} \tag{24}$$

If $k_{TS}(E)$ is a good approximation to $k(E)$ up to an energy E' many kT above the classical threshold for reaction, the mutilated integral

$$k_{TS}^{E'} = Q^{-1} \int^{E'} dE \, k_{TS}(E) \exp(-E/kT) \tag{25}$$

is a good approximation to the correct thermal rate constant k [Eq. (22a)].

Notice that $k_{TS}(E) \geq k(E)$, for if $\mathbf{p} \cdot \mathbf{n}_s > 0$, we have $\chi_+(\mathbf{p}, \mathbf{q}_s, \mathbf{n}_s) = 1$ by definition but $\chi_r(\mathbf{p}, \mathbf{q}_s)$ may be zero, whereas if $\mathbf{p} \cdot \mathbf{n}_s < 0$, we have $\chi_+(\mathbf{p}, \mathbf{q}_s, \mathbf{n}_s) = 0$ by definition but $\chi_r(\mathbf{p}, \mathbf{q})$ may be unity. Transition state theory, then, may be looked on as a variational theory of reaction rates[11]: One attempts to minimize the transition state rate contant by varying the transition state, with the assurance that one can never underestimate the thermal rate constant.

The best choice of transition state in the one-dimensional model of the previous section was the point of highest potential energy between reactants and products. On the typical two-dimensional potential surface, with a single saddle point in the interaction region, the minimum of $V(\mathbf{q}_s)$ along any curve $\mathbf{q}_s$ separating reactants from products must be less than or equal to the saddle point energy, so for the sake of energy it would seem that the best transition state should pass through the saddle point and then climb the potential wall on either side as quickly as possible, that is, along the "path of steepest ascent" that follows the gradient of the potential. But it is not necessarily so. In two dimensions we want a transition state that is both high and narrow. The reader should ponder the potential maps of Figs. 5 and 6 to understand why in some cases entropic considerations—the length of the transition state—may shift the best transition state well off the saddle point.

As always, entropy is more important the higher the temperature, and for that matter classical mechanics is more accurate the higher the temperature, so
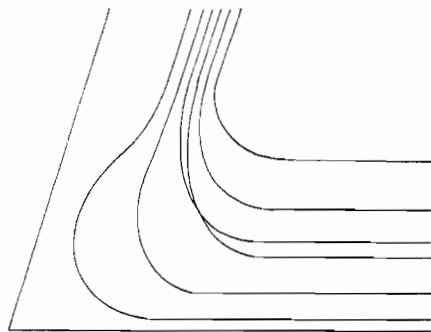

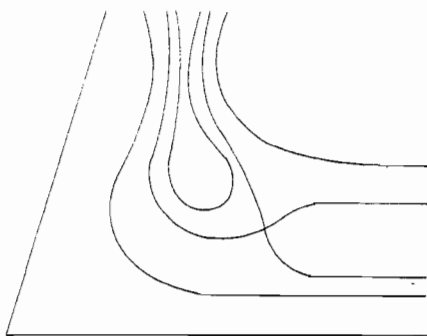Fig. 5. Where is the transition state?

Fig. 6. Where is the transition state?

there is still interesting work to do on classical variational rate theory in high-temperature chemistry.

In the two-dimensional model of this section we can go fairly far with the problem of finding the "best" transition state. Return to Eqs. (22) and (23) defining microcanonical (single-energy) rate constants and their transition state approximants. Equation (22b) gives $k(E)$ independent of the curve $\mathbf{q}_s$, and no matter how we choose $\mathbf{q}_s$, $k_{TS}(E)$ can be no smaller than $k(E)$. We may in fact pick the best transition state for each energy—a different curve $\mathbf{q}_s$ for every E. Now to get reaction the total energy of the system must exceed the potential energy at the saddle point, and at any energy above the saddle point energy we shall usually have only two equipotentials, running along on either side of the saddle point. Draw a curve $\mathbf{q}_s$ from one equipotential to the other (Fig. 7); any reactive trajectory of energy E must cross this curve. If we have happened by chance to pick the curve $\mathbf{q}_s$ for which the value of $k_{TS}(E)$ is a minimum, we must have [from Eq. (24)]

$$\delta \int_1^2 ds[E - V(\mathbf{q}_s)]^{1/2} = 0 \tag{26}$$

for all variations in curve leading from 1 to 2. We recognize Eq. (26) as one of the variational formulations of classical mechanics[12]; the curve $\mathbf{q}_s$ must be the
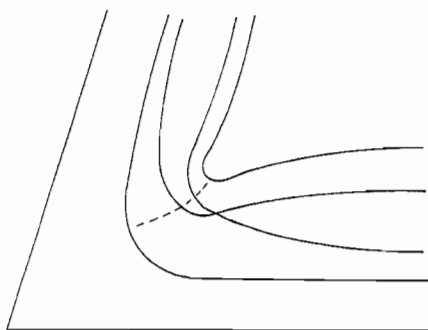
Fig. 7. Anharmonic vibration across the saddle point region (– –).

orbit of a classical trajectory, of total energy E, between points 1 and 2. The best transition state at given energy lies along a "vibration" of the system between the two equipotentials of that energy. Notice that at the end points, where $E = V$, the particle comes to a halt and therefore starts off at points 1 and 2 in the direction of the force: $\mathbf{q}_s$ meets the two equipotentials at right angles.

Do such vibrations exist? Certainly. In the immediate vicinity of the saddle point the potential may be expanded to quadratic terms in displacement from the saddle point, and at energies just above the saddle point energy the appropriate vibration is harmonic and in a straight line directly through the saddle point. At a higher energy we start a particle off with velocity zero on one of the equipotentials, somewhere in the neighborhood of the saddle point. It heads out toward the other equipotential but perhaps does not make it, falling away from the saddle point region in, say, the product direction. We move over and start the particle off on the equipotential again; now we find that it falls away to the reactant side. Somewhere between these two trajectories is a "dividing" trajectory that falls away neither to reactant nor to product; this is the required "vibration," across the saddle point region but not necessarily through the saddle point, and the curve executed on the plane by the vibration is the best transition state at that energy. (At least, it is the best in the vicinity of the saddle point. The potential surface may allow other such vibrations. Find one in Fig. 6 and convince yourself that at high energy it is the transition state of choice.)

As in one dimension, the best transition state is a state of dynamical instability. The vibration linking two equipotentials separates motion of qualitatively different character: A little push off to one side and we get reactant, a push to the other side and we get product.

The best transition state may of course be rather bad: The accuracy of the transition state approximation must depend on the details of the potential surface. Numerical calculations[13] on the Porter–Karplus $H + H_2$ surface[14] have shown that the transition state rate constant $k_{TS}(E)$ is an excellent approximation to the exact $k(E)$ up to energies 10–20 kcal/mole above the saddle point. It is interesting to ask why transition state theory is so good for this surface, and, more generally, how we can recognize surfaces for which transition state theory will be accurate.

We saw above that the necessary and sufficient condition that transition state theory be exact at energy E is that $\chi_+ = \chi_r$ for all phase points of energy E on the transition state. This is a dynamic condition and may be put in more picturesque terms as follows: $\chi_+ = \chi_r$ if and only if every trajectory that leaves the transition state never returns. The essential point here is that if a trajectory crosses the transition state and returns to cross it again the sign of $\mathbf{p} \cdot \mathbf{n}$—and therefore the value of χ_+—differs at the two crossings, whereas χ_r is constant along the entire trajectory and therefore must differ from χ_+ at one of the crossings.

It is instructive to examine the characterization given above of the best transition state at given energy in terms of the dynamic criterion that a trajectory leaving the transition state should not return. If the transition state is *not* the orbit of a classical trajectory, we can be certain that there exist trajectories that leave the transition state only to return and cross it again. For example, suppose that a phase point starts off at time zero along the transition state but falls away to, say, the product side by time t; classical position and momentum at time t are continuous functions of classical position and momentum at time zero, so there is a phase space neighborhood of the original phase point all of whose trajectories reach the product side by time t, and this neighborhood necessarily contains points on the transition state with momentum initially directed to the reactant side. Transition state theory is automatically incorrect, then, unless trajectories that start along the transition state remain on it for all time.

One can check whether or not transition state theory is exact at energy E by following all trajectories that leave the transition state with that energy and observing whether they return, but this is essentially a complete dynamical calculation. There is a simple geometric condition on potential surfaces sufficient (but not necessary!) to ensure that transition state theory is exact at all energies below a given energy E.[15] Suppose that we can draw a *straight* line through the saddle point and perpendicular to all the equipotentials up to energy E; this will be the transition state, the same for all energies $\leqslant E$. Consider the band of the plane lying between the two equipotentials at energy E, and suppose that we can cover the entire band with a family of straight lines in such a manner that the force $-\nabla V$, at any point on any of these straight lines, never lies to the transition state side of the line. Then no trajectory with energy less than or equal to E, and coming from the transition state, can ever return. The essence of the proof is that such a trajectory would have to "turn back" at a point of tangency to one of these straight lines, and it cannot do so if the forces will not help.

In practice this is an easy criterion to test. We have only to move a ruler over the map of the equipotentials, adjusting continuously as we go from
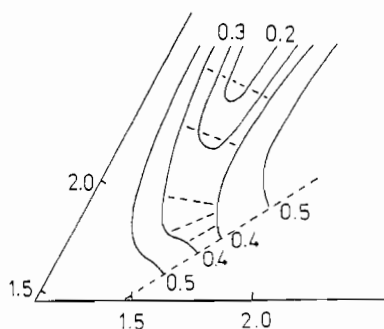

Fig. 8. Equipotentials on the Porter–Karplus H_3 surface. Energies in electron volts, distances in atomic units.

transition state to product or from transition state to reactant and checking whether the equipotentials can be made to "open out" as they cross the straightedge or, at worst, run perpendicular to the straightedge. Figure 8 illustrates the test on the Porter–Karplus H_3 surface, where symmetry ensures a straight transition state; we show typical members of a family of straight lines linking the 0.4 eV equipotentials, and the forces clearly lie as desired, so transition state theory is exact on the Porter–Karplus surface at least up to 0.4 eV (no great achievement, because the saddle point is at 0.396 eV).

Transition state theory is exact, then, if the potential surface "expands" in a well-defined sense as we move away from the transition state, in either product or reactant direction. This is just what one expect physically: Transition state theory is a theory for systems with a genuine "bottleneck" to reaction.

2.4. Multidimensional Potential Surfaces: Saddle Points, Counting Problems, and the Conservation of Nuclear Symmetry along Reaction Paths

We return to the general bimolecular reaction $A + B \rightleftharpoons C + D$. To calculate the exact equilibrium rate constant we need the characteristic function of reactive trajectories—trajectories that are separated $A + B$ in the indefinite past and separated $C + D$ in the indefinite future—and a surface, any surface, separating the asymptotic reactant and product regions in the N-atom phase space of the colliding pair. The rate constant is then proportional to the flux of the density $\chi_r \exp(-H/kT)$ across this surface, per unit volume allowed to the center of mass of the system. Transition state theory instructs us to approximate the reactive flux across the surface by the total thermal flux from reactant to product side and then to vary the surface until the best—that is, least—transition state rate is obtained.

This is easier said than done: There are many surfaces in phase space. Variational theory of reaction rates is hard enough in two dimensions and much more so in the real world even for a three-atom exchange reaction. Accordingly, we shall not dwell on the variational aspect of transition state theory in its most general setting.* The lesson of Section 2.3 is that when the potential "expands" in either direction away from a saddle point the best choice of transition state lies in the neighborhood of the saddle point and transition state theory can be quite accurate, so in this section we shall discuss saddle points on multidimensional potential surfaces and related matters of importance to rate theory.

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*The interested reader should consult Keck's excellent 1967 review[11] for a full discussion of variational theory and for methods of calculating flux through a general surface in phase space. Also of interest is a recent article by Jaffe et al. on the $F + H_2$ reaction[16] in which the authors strike a compromise by choosing not the best surface but one easy to work with and supplement variational theory with exact trajectory calculations (see the remarks at the end of this section).

Let $V(\mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_N)$ be the potential energy of the N-atom system as a function of the positions $\mathbf{q}_1, \ldots, \mathbf{q}_N$ of the various atoms; we write $V(\mathbf{q}_1, \ldots, \mathbf{q}_N) \equiv V(\mathbf{q})$ for brevity. A stationary point of the potential is a point at which all first derivatives vanish: $\nabla V(\mathbf{q}) = 0$, where ∇ is the gradient operator in $3N$-dimensional configuration space.

We classify stationary points according to the eigenvalues of the symmetric $3N \times 3N$ matrix of mixed second derivatives of V at $\mathbf{q}$. Some of the eigenvalues will be zero, at least five if the stationary point is a linear configuration (i.e., $\mathbf{q}_1, \ldots, \mathbf{q}_N$ all lie on a line) and at least six otherwise, for the potential is unchanged by translation or rotation of the system as a whole, and if $(\mathbf{q}_1, \ldots, \mathbf{q}_N)$ is a stationary point, so is $(\mathbf{q}_1 + \mathbf{a}, \ldots, \mathbf{q}_N + \mathbf{a})$ and $(R\mathbf{q}_1, \ldots, R\mathbf{q}_N)$, where $\mathbf{a}$ is any vector and R any rotation. The matrix may have negative eigenvalues. If there are none, the stationary point $\mathbf{q}$ is called a minimum, and in the immediate vicinity of $\mathbf{q}$ there is no direction in $3N$-dimensional configuration space along which the potential decreases. If the matrix has one negative eigenvalue, the stationary point $\mathbf{q}$ is called a simple saddle point, and there is one direction along which the potential is parabolic downward. If there are two negative eigenvalues, $\mathbf{q}$ is a double saddle point, and so on up to the case of no positive eigenvalues: a potential maximum.

Stable molecular configurations are minima, transition states are simple saddle points, and rate theory avoids all higher-order saddle points for reasons that will be clear in a moment.

A potential surface is a function of all possible configurations of the N-atom system, and any conceivable rearrangement process involving the N atoms may occur on the surface; to which reaction does a given simple saddle point "belong"? We find out by following the "reaction path," defined loosely as the path of steepest descent from the saddle point and more formally as the path that follows the gradient of the potential away from the saddle point:

$$d\mathbf{q}/ds = -\nabla V(\mathbf{q})/|\nabla V(\mathbf{q})| \tag{27}$$

where s is arc length along the path. The reader should not confuse a solution of Eq. (27) with the transition state curves $\mathbf{q}_s$ of the preceding section or with solutions of Newton's equation. There is no dynamics here. The reaction path as defined by Eq. (27) is just a useful mathematical device for going from high ground, at the saddle point, to low ground, where the stable molecules are.

The reaction path through a simple saddle point in two dimensions is shown in Fig. 4.

One aspect of the mathematical theory of Eq. (27) is quite important. Notice that the right-hand side of the equation is indeterminate at a stationary point, where $\nabla V = 0$, so there is the possibility of many solutions to Eq. (27) emanating from a given stationary point. From a simple saddle point, however, there are only two solutions along which the potential decreases as we go out from the saddle point; the solutions start off in opposite directions along the

"principal axis" with negative eigenvalue defined by the expansion of V to second order about the saddle point. The reader who is unconvinced of this should sketch the force field around a simple saddle point in two dimensions or examine the behavior of solutions to Eq. (27) in the immediate vicinity of a simple saddle point, where the quadratic approximation is sufficient.

The two sections of reaction path will proceed out from the saddle point according to Eq. (27) until each reaches another stationary point at which $\nabla V = 0$ and the equation is again indeterminate. Usually each piece of the reaction path will by then have gotten outside the region in which all N atoms are close together, and the configuration described by one piece will be, say, separated $A + B$ and by the other piece will be separated $C + D$. We have found a saddle point appropriate to the $A + B \rightleftharpoons C + D$ reaction.

What happens at a double saddle point? Then—quite apart from the fact that the approximate formulas below have no meaning—there is in general no unique reaction to which the saddle point belongs: Equation (27) has an infinite number of solutions passing through the saddle point and along which the potential decreases. A double saddle point is a "hill" with respect to the two directions in which the potential decreases, and we have to grope around the base of the hill until we locate some simple saddle points.

The contribution of a simple saddle point to the rate of the reaction to which it belongs is easy to calculate if the harmonic oscillator–rigid rotor approximation applies in the "thermal neighborhood" of the saddle point. We require that the potential be well approximated by an expansion to quadratic terms, along the directions in which the potential is parabolic upward, to an energy a few kT in excess of the saddle point energy and also that the atomic displacements necessary to raise the energy a few kT along these directions be small compared to the interatomic distances at the saddle point, so that we have essentially a rigid configuration of atoms. Then to describe the motion of the system in the thermal neighborhood of the saddle point it suffices to expand the potential to quadratic terms about the saddle point and make a standard transformation to normal coordinates (see any textbook on classical mechanics for the details). The Hamiltonian in normal coordinates is a sum of $3N$ independent harmonic oscillator Hamiltonians. The vibrational frequency associated with one normal coordinate, the so-called "reaction coordinate," will be imaginary: The potential is parabolic downward in this direction, which lies more or less (depending on the atomic masses) along the reaction path. The vibrational frequency associated with five (if the saddle point configuration is linear) or six (nonlinear) normal coordinates will be zero: an infinitesimal displacement along these coordinate directions is an infinitesimal translation-rotation of the saddle point configuration, with no change in potential energy. The vibrational frequencies associated with the other normal coordinates— $3N - 6$ if the saddle point is linear and $3N - 7$ otherwise—will all be positive if the simple saddle point occurs in the region of interaction where all N atoms are close together.

Now we must choose the best transition state in the saddle point region. The lesson of Sections 2.2 and 2.3 is that the best transition state is a set of classical trajectories. This fixes it right off: We set the reaction coordinate and momentum to zero, and then we have rigid rotation–translation and harmonic vibrations in the remaining $3N - 1$ degrees of freedom, an unstable "molecule" that hangs around forever if nothing disturbs it.

In the neighborhood of a simple saddle point, variational reaction rate theory leads us right back to the elementary derivation of Section 2.1. In the immediate vicinity of the transition state we have a Hamiltonian as in Eq. (5), with p and m^* the momentum and mass along the reaction normal coordinate, and the partition function of the transition state is calculated just as for an ordinary molecule in the harmonic oscillator–rigid rotor approximation, with one vibration missing. This is a standard calculation, and we shall simply quote the results. We shall have a product of translational, rotational, and vibrational partition functions. If the saddle point configuration is linear,

$$Q^{\ddagger} = \left(\frac{2\pi MkT}{h^2}\right)^{3/2} \frac{8\pi^2 IkT}{h^2} e^{-E^*/kT} \prod_{i=1}^{3N-6} \frac{kT}{h\nu_i} \tag{28}$$

where M is the total mass of the N-atom system, I the moment of inertia about the center of mass, E^* the potential energy at the saddle point, and ν_i the various frequencies of vibration; if the saddle point configuration is nonlinear,

$$Q^{\ddagger} = \left(\frac{2\pi MkT}{h^2}\right)^{3/2} \pi^{1/2} \prod_{j=1}^{3} \left(\frac{8\pi^2 I_j kT}{h^2}\right)^{1/2} e^{-E^*/kT} \prod_{i=1}^{3N-7} \frac{kT}{h\nu_i} \tag{29}$$

where the I_j are the principal moments of inertia of the saddle point configuration.

The reader familiar with the usual high-temperature approximation of molecular partition functions, which is in essence what a classical partition function is, will notice that Eqs. (28) and (29) lack nuclear spin degeneracies and symmetry numbers. Nuclear spin degeneracies can be ignored: The nuclei are the same in the transition state as in reactants or products, and the degeneracies cancel on top and bottom in the expression for the rate constant.

Symmetry numbers are another matter. It is possible to construct seeming paradoxes in rate theory by postulating transition states of particular symmetry for families of similar reactions where one knows from common sense the relative rates, and there has been discussion and some confusion in the literature as to whether one should use symmetry numbers for transition states in the same manner as for stable molecules.† Briefly, the answer is yes, absolutely. One cannot tamper with the laws of statistical thermodynamics, and the partition function of the transition state has to be evaluated in standard manner or the concentration of transition state intermediates at equilibrium

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†See the text by Laidler[3] for an extensive and excellent discussion of the problem.

will not come out right; and if one has the concentration of transition state intermediates correct, the calculation in Section 2.1 of the rate at which they disappear to become product is flawless, within the dynamic approximation that a system that leaves the transition state can never return. But one has to be certain that a proposed reaction intermediate can in fact be a simple saddle point on the potential surface so that the theory will make sense (we shall see in a moment that there are severe restrictions on the symmetry of transition states), and one also has to be sure to find *all* transition states linking reactant and product, for all contribute to the rate.

Symmetry numbers are a concern when the N atoms of colliding pair A + B are not all different: We may have many hydrogens, a couple of oxygens, a mess of carbons, and so on. The potential is unchanged by any permutation of the positions of identical atoms, and therefore if $\mathbf{q}$ is a stationary point of the potential, so is any point obtained from $\mathbf{q}$ by a permutation of identical atoms: If the system contains n_i atoms of type i, we have automatically $\Pi_i n_i!$ stationary points, differing only in the numbering of identical atoms. Atomic arrangements differing only in the numbering of identical atoms are to be counted as the same molecule. However, we cannot automatically add all $\Pi_i n_i!$ contributions of the form (28) or (29) to the partition function of the arrangement defined by $\mathbf{q}$, for some of these stationary points may be obtained from $\mathbf{q}$ by rotation and therefore may already have been "counted" in the partition function assigned to $\mathbf{q}$. Specifically, let $\sigma - 1$ be the number of permutations of $\mathbf{q}$ that can be reached from $\mathbf{q}$ by a smooth curve, in $3N$-dimensional configuration space, along which the potential does not change; σ is the symmetry number of the atomic arrangement defined by $\mathbf{q}$. If $\mathbf{q}$ is an arrangement in which the N atoms are all close, as in a transition state, the only permutations of $\mathbf{q}$ that we can reach without changing the potential energy along the way are those obtained by rigid rotation of the N-atom arrangement. If $\mathbf{q}$ is a stationary point representing separated A and B, we can rotate A and B independently, and it is easy to see that the symmetry number of $\mathbf{q}$ is the product $\sigma_A \sigma_B$ of the symmetry numbers of isolated A and B.

We shall obtain a contribution of the form (28) or (29) to the partition function of the atomic arrangement defined by $\mathbf{q}$ for each *distinct* stationary point in the collection of $\mathbf{q}$ and its permutations; the number of such contributions is $\Pi_i n_i!/\sigma$. The ratio $Q^{\ddagger}/Q_A Q_B$ in the transition state rate constant is therefore equal to $(Q_1^{\ddagger}/Q_{1A}Q_{1B})(\sigma_A \sigma_B/\sigma^{\ddagger})$, where the Q_1 are partition functions associated with a *single* stationary point.

Methane is a useful molecule on which to exercise one's understanding of symmetry numbers. There are four equivalent hydrogens at the potential minimum. The number of minima related by permutation is $4! = 24$; the symmetry number is 12 (four threefold axes and three twofold axes); and so there are two distinct potential minima, one related to the other by reflection in the plane of two C—H bonds.

Question: Suppose that the Lord suddenly arranges, for pedagogic purposes, that at the potential minimum all four C—H bonds differ slightly in length by a few millionths of an Angstrom and that the symmetry number of methane becomes 1; does industry's chance of finding natural gas in an equilibrium mixture of hydrocarbons suddenly jump 12-fold? The answer is no: Distinct stationary points contribute independently to the partition function of an atomic arrangement only if the thermal neighborhoods of each do not overlap, and in this case we can go from 1 potential minimum to 11 others by a combination of rotation and change in bond length without changing the potential energy by anything approaching kT. Therefore caution is necessary: The distinct stationary points contributing to the partition function of a given atomic arrangement, whether stable molecule or transition state, must be truly distinct.

In a rate calculation we have to sum over all transition states connecting reactants and products. The saddle point of lowest energy (together with all its permutations) will usually dominate the rate, but there will be two such points if the saddle point configuration is optically active (that is, if the atomic configuration produced by reflecting the saddle point configuration in a plane cannot be made to coincide with the original configuration by any rotation). If the reactants and products are optically inactive, we shall have two contributions to the rate, from the saddle point enantiomers, equal in magnitude because the potential energy of an atomic configuration is not altered by reflection in a plane. We leave it to the reader to reflect on the various possibilities when reactants and/or products are optically active, bearing in mind that a given transition state configuration must lead to a unique configuration of reactants and products; for counting purposes, it is simplest to treat enantiomers as geometrical isomers—i.e., different molecules—just as one distinguishes and bottles and sells the various forms of hexane although all lie on the same potential surface.

As every organic chemist knows, an optically *inactive* transition state cannot connect optically active reactants and products. This is the most trivial consequence of a general result on conservation of symmetry along reaction paths that we shall now discuss.*

We label the nuclei 1 through N (indistinguishable nuclei are nevertheless given different labels), and in the potential function $V(\mathbf{q}_1, \mathbf{q}_2, \cdots, \mathbf{q}_N)$ the first entry $\mathbf{q}_1$ refers always to the position of nucleus 1, the second entry $\mathbf{q}_2$ to the

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*References for this discussion of nuclear symmetry are Pearson[17] and Metiu et al.[18] Both observe that ∇V has the symmetries of the configuration at which it is evaluated. Pearson concludes that nuclear symmetry is preserved along a reaction path until a stationary point is reached. Metiu et al. disagree, essentially because they do not accept Eq. (38) as the definition of the reaction path. They raise the possibility of interesting complications that we shall not consider here: First, in our language, the possibility that the solution of Eq. (38) is unstable—a little push off to one side and the reaction path finds an entirely new set of reactants or products; second, the possibility that a given set of reactants and products may not be linked by any solution of Eq. (38).

position of nucleus 2, and so on. We define permutation and rotation–reflection operators in the $3N$-dimensional configuration space as follows. If P is a permutation of identical nuclei—for instance,

$$P = \begin{pmatrix} 1 & 2 & 3 & \cdots & 7 & \cdots \\ 3 & 2 & 7 & \cdots & 1 & \cdots \end{pmatrix} \tag{30}$$

in standard notation—then

$$P(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3, \ldots, \mathbf{q}_7, \ldots) = (\mathbf{q}_3, \mathbf{q}_2, \mathbf{q}_7, \ldots, \mathbf{q}_1, \ldots) \tag{31}$$

If R is a rotation or reflection in three-dimensional space, then

$$R(\mathbf{q}_1, \mathbf{q}_2, \ldots) = (R\mathbf{q}_1, R\mathbf{q}_2, \ldots) \tag{32}$$

In the same manner we define P and R acting on an arbitrary $3N$-component vector $\mathbf{v} = (\mathbf{v}_1, \mathbf{v}_2, \ldots)$:

$$P\mathbf{v} = (\mathbf{v}_3, \mathbf{v}_2, \mathbf{v}_7, \ldots, \mathbf{v}_1, \ldots), \qquad R\mathbf{v} = (R\mathbf{v}_1, R\mathbf{v}_2, \ldots) \tag{33}$$

P and R are linear operators, commute with each other, and preserve dot products:

$$P\mathbf{u} \cdot P\mathbf{v} = \mathbf{u} \cdot \mathbf{v}, \qquad R\mathbf{u} \cdot R\mathbf{v} = \mathbf{u} \cdot \mathbf{v} \tag{34}$$

The potential is invariant under any P or R:

$$V(P\mathbf{q}) = V(\mathbf{q}), \qquad V(R\mathbf{q}) = V(\mathbf{q}) \tag{35}$$

It follows that

$$P\boldsymbol{\nabla} V(\mathbf{q}) = \boldsymbol{\nabla} V(P\mathbf{q}), \qquad R\boldsymbol{\nabla} V(\mathbf{q}) = \boldsymbol{\nabla} V(R\mathbf{q}) \tag{36}$$

for if $d\mathbf{q}$ is any infinitesimal displacement, we have

$$\boldsymbol{\nabla} V(P\mathbf{q}) \cdot P\,d\mathbf{q} = V[P(\mathbf{q} + d\mathbf{q})] - V(P\mathbf{q}) = V(\mathbf{q} + d\mathbf{q}) - V(\mathbf{q})$$

$$= \boldsymbol{\nabla} V(\mathbf{q}) \cdot d\mathbf{q} = P\boldsymbol{\nabla} V(\mathbf{q}) \cdot P\,d\mathbf{q} \tag{37}$$

$$\boldsymbol{\nabla} V(R\mathbf{q}) \cdot R\,d\mathbf{q} = \cdots = R\boldsymbol{\nabla} V(\mathbf{q}) \cdot R\,d\mathbf{q}$$

and this can be true for arbitrary $d\mathbf{q}$ only if Eq. (36) holds.

Now consider the equation by which we define reaction paths,

$$d\mathbf{q}/ds = -\boldsymbol{\nabla} V(\mathbf{q})/|\boldsymbol{\nabla} V(\mathbf{q})| \tag{38}$$

$\mathbf{q}(s)$ follows along the gradient of the potential, and V decreases as the arc length s increases. There is a solution of Eq. (38) passing through any point $\mathbf{q}(s') \equiv \mathbf{q}'$ at which $\boldsymbol{\nabla} V(\mathbf{q}') \neq 0$, unique as long as $\boldsymbol{\nabla} V[\mathbf{q}(s)] \neq 0$. Further, if $\mathbf{q}(s)$ is a solution of Eq. (38), so are $P\mathbf{q}(s)$ and $R\mathbf{q}(s)$; for instance,

$$dP\mathbf{q}(s)/ds = -P\boldsymbol{\nabla} V(\mathbf{q})/|\boldsymbol{\nabla} V(\mathbf{q})| = -\boldsymbol{\nabla} V(P\mathbf{q})/|\boldsymbol{\nabla} V(P\mathbf{q})| \tag{39}$$

R is a symmetry of the point $\mathbf{q}$ if there is a permutation P such that $PR\mathbf{q} = \mathbf{q}$—in other words, if $\mathbf{q}$ and $R\mathbf{q}$ differ only in the labeling of indistinguishable particles. Consider a solution of Eq. (38) on which $\boldsymbol{\nabla} V[\mathbf{q}(s)] \neq 0$ and

$$\frac{d}{ds}\, PRq(s) = PR\frac{1}{ds} = -PR\frac{\partial V(q)}{|\partial V(q)|} = -P\frac{\partial V(Rq)}{|\partial V(Rq)|} = -\frac{\partial V(PQ)}{|\partial V(PQ)|}\, \frac{\partial V(PRq)}{|\partial V(PRq)|}$$

let $Rq = q'$ then

suppose that R is a symmetry of one point lying on $\mathbf{q}(s)$—say, $\mathbf{q}(s') \equiv \mathbf{q}'$. Then R is a symmetry of all points $\mathbf{q}(s)$, for $\mathbf{q}(s)$ and $PR\mathbf{q}(s)$ are both solutions of Eq. (38) and both pass through $\mathbf{q}'$; by uniqueness of the solution through $\mathbf{q}'$, they must in fact be identical. Symmetry is preserved along solutions of Eq. (38) as long as we do not meet a point at which $\nabla V = 0$.

What happens if $\nabla V(\mathbf{q}_0) = 0$ and $\mathbf{q}(s) \to \mathbf{q}_0$ as $s \to s_0$? If R is a symmetry of the path $\mathbf{q}(s)$, R must be a symmetry of the point $\mathbf{q}_0$, by continuity, for

$$\mathbf{q}_0 = \lim_{s \to s_0} \mathbf{q}(s) = \lim_{s \to s_0} PR\mathbf{q}(s) = PR\mathbf{q}_0 \qquad (40)$$

The point $\mathbf{q}_0$ may have other symmetries *not* shared by the path $\mathbf{q}(s)$ of which it is a limit point: If R' is a symmetry of $\mathbf{q}_0$, $P'R'\mathbf{q}_0 = \mathbf{q}_0$, the path $P'R'\mathbf{q}(s)$ is a solution of Eq. (38) with limit $\mathbf{q}_0$, but this solution does not necessarily coincide with $\mathbf{q}(s)$, for there are in general *many* solutions of Eq. (38) passing through $\mathbf{q}_0$. The limit $\mathbf{q}_0$ is a point of indeterminacy for Eq. (38): A solution does not "know" in what direction to start.

Consider, however, the case where $\mathbf{q}_0$ is a simple saddle point. Then there are only two solutions of Eq. (38) starting at $\mathbf{q}_0$, one leading to reactants and one to products. If R is a symmetry of the saddle point, $PR\mathbf{q}_0 = \mathbf{q}_0$, and $\mathbf{q}(s)$ leads down to reactants, the path $PR\mathbf{q}(s)$ also starts at $\mathbf{q}_0$, satisfies Eq. (38), and must therefore coincide with $\mathbf{q}(s)$ or with the second path, leading to products. The latter is a possibility only if the reaction is a symmetric exchange, $A + B \rightleftharpoons B + A$ (that is, no reaction at all); in this case the transition state may have more symmetry than points on the reaction path, as in the collinear $H + H_2$ reaction where the saddle point has a center. Otherwise, a symmetry of the transition state is a symmetry of the entire reaction path.

Transition state theory requires a simple saddle point as intermediate between reactants and products; the symmetry of the saddle point must be maintained at all points along the reaction path leading from reactants through the saddle point to products; therefore—and most important—the reactant and product configurations reached along the reaction path can have no less symmetry than the transition state.

This is in fact a severe restriction on mechanisms of reactions that proceed through a simple saddle point. The most immediate consequences are that linear transition states must give linear reactants and products, planar transition states must give planar reactants and products, and optically inactive transition states must give optically inactive reactants and products. Much more is true, because the reactant and product configurations are separated molecules, and there are not many symmetries available to a pair of spatially separated groups of atoms. We leave aside the case of a symmetric exchange, discussed above, and isomerization reactions of the form $A + A \rightleftharpoons B + B$. Then a transition state can have only one axis of rotation, for the only symmetry axis

available to separated molecules that are not identical is a line through the centers of mass of the molecules. Similarly, the only reflections possible are through planes containing the centers of mass of the separated molecules. Finally, and most important, a symmetry of separated reactants and products can interchange indistinguishable particles only within the same molecule. In any proposed mechanism for the reaction $A + B \rightarrow C + D$—that is, any proposed reaction path from reactants to products—we can label each of the nuclei with one of the four pairs (A, C), (A, D), (B, C), (B, D) to indicate the reactant and the product molecule to which the nucleus belongs. Only those rotations or reflections that interchange nuclei with the same labels are allowed.

This ends our discussion of classical transition state theory per se. However, the notion of a "transition state"—a surface in the region of interaction through which every reactive trajectory must pass—has other uses, especially in the design of efficient classical dynamical calculations of exact thermal rate constants, final state distributions produced in reaction, and so on.[16] We need the characteristic function of reactive trajectories, $\chi_r(\mathbf{p}, \mathbf{q})$. If we attempt a Monte Carlo calculation of χ_r by sampling trajectories that start in the asymptotic reactant region, we often find that remarkably few trajectories manage to react. By contrast, if we start trajectories on a cleverly chosen transition state and integrate both forward and backward in time to determine their entire history, we can reasonably expect a far higher percentage of reactive trajectories and therefore a more rapid calculation of χ_r.

We shall close this section by emphasizing an elementary point about the distributions generated by χ_r. The probability distribution of reactive phase points on the transition state is $\chi_r \exp(-H/kT)$, *not* an equilibrium distribution: Each phase point carries the Maxwell–Boltzmann weight $\exp(-H/kT)$, but only phase points lying on reactive trajectories are "populated." If transition state theory is exact and χ_r is equal to the characteristic function of phase points about to leave the transition state to the product side, we have half an equilibrium distribution at the transition state. But even in this well-behaved case there is no assurance that the products produced in the reaction will be anywhere near equilibrium. Final state distributions are governed by the function $\chi_r \exp(-H/kT)$ in the asymptotic product region; again, each phase point carries its Maxwell–Boltzmann weight, but again only those phase points lying on reactive trajectories are populated. The energy released as products separate may go largely into product vibration or largely into product rotation or largely into product translation, depending on the shape of the potential surface from the transition state to the asymptotic product region.

We may also ask for the distribution of reactants *leading to reaction*. This is governed by the function $\chi_r \exp(-H/kT)$ in the asymptotic reactant region, and reaction may require mainly vibrational or mainly rotational or mainly translational energy, depending on the shape of the potential surface between the transition state and the asymptotic reactant region.

Transition state theory of direct reactions says nothing about initial and final state distributions. The distribution may be exactly equilibrium at the transition state, on phase points about to become product, but reaction may nevertheless proceed from a highly nonequilibrium distribution of reactants to a highly nonequilibrium distribution of products.

3. Quantum Transition State Theory of Direct Reactions

3.1. The Separable Approximation

To make a quantum transition state theory we reason that quantum effects should be more important the lower the temperature, and the lower the temperature the more the rate should be dominated by saddle points on the potential energy surface. Clearly we want to replace classical partition functions with quantum partition functions. In Eqs. (28) and (29) we can leave the rotational partition functions alone unless we are at very low temperature or have reactants and/or transition states with small moments of inertia. Vibrations are another matter; vibrational partition functions should certainly be evaluated quantum mechanically,

$$\prod_i \frac{kT}{h\nu_i} \rightarrow \prod_i \frac{\exp(-h\nu_i/2kT)}{1-\exp(-h\nu_i/kT)} \equiv \prod_i \frac{kT}{h\nu_i}\left[\frac{h\nu_i/2kT}{\sinh(h\nu_i/2kT)}\right] \qquad (41)$$

The term $(h\nu_i/2kT)/\sinh(h\nu_i/2kT)$ can be regarded as "quantum correction" to the vibrational partition function of the ith normal mode. It is an enormous "correction": At room temperature thermal energy is about $200\,\text{cm}^{-1}$, whereas vibrational energies range up to $3000\,\text{cm}^{-1}$ or more.

This is not the only quantum correction necessary. The rate at which systems cross the transition state, from reactant to product side along the reaction coordinate, yields the classical factor kT/h in the rate expression (8); quantum mechanically there is the possibility of tunneling through the saddle point barrier at energies below the classical threshold, as well as the possibility of reflection at energies above the classical threshold. To correct for these effects we look at the classical calculation:

$$\frac{kT}{h} = h^{-1}\int_0^\infty dp\,\frac{p}{m}\exp\left(-\frac{p^2}{2mkT}\right) = h^{-1}\int_0^\infty dE\,\exp\left(-\frac{E}{kT}\right)$$

$$= h^{-1}\int dE\,P(E)\exp\left(-\frac{E}{kT}\right) \qquad (42)$$

where $P(E)$ is the classical probability of crossing the saddle point barrier at an

energy E measured with respect to the barrier maximum, $P(E) = 1$ if $E > 0$ and zero otherwise. This suggests that we replace $P(E)$ by the quantum probability of crossing the barrier at energy E, integrating over all energies for which barrier passage is possible. Because we are looking in the immediate vicinity of the saddle point, the barrier to reaction is parabolic downward along the reaction normal coordinate q, and the potential, as a function of reaction coordinate, is characterized by an "imaginary frequency" $i\nu^*$:

$$V(q) = m^*(2\pi i\nu^*)^2 q^2/2 \qquad (43)$$

where m^* is the mass associated with motion along the reaction coordinate in the vicinity of the saddle point. We reason, in the saddle point spirit, that only small q count and use the barrier passage probability $P(E)$ for the infinite parabolic barrier [Eq. (43) for all q]. $P(E)$ is nonzero for all E [because $V(q)$ goes down to $-\infty$ as $q \to \pm\infty$] and has the value[19]

$$P(E) = [1 + \exp(-2\pi E/h\nu^*)]^{-1} \qquad (44)$$

The integral

$$h^{-1} \int_{-\infty}^{+\infty} dE \frac{\exp(-E/kT)}{1 + \exp(-2\pi E/h\nu^*)} \qquad (45)$$

is not difficult (integrate in the complex energy plane around the rectangle with corners at $E = \pm\infty$, $\pm\infty + ih\nu^*$, and do not forget the pole at $E = ih\nu^*/2$). Instead of the classical factor kT/h, we obtain

$$\frac{kT}{h} \frac{h\nu^*/2kT}{\sin(h\nu^*/2kT)} \qquad (46)$$

There is a marvelous symmetry here. The quantum correction for the reaction coordinate is the same as for the vibrational coordinates; it is just that the associated "vibrational frequency" is imaginary. However, there is an important difference between the functions $x/\sinh x$ and $x/\sin x$: The latter blows up every so often. In fact, the integral (45) diverges for any temperature below $h\nu^*/2\pi k$: The Maxwell–Boltzmann factor increases with decreasing energy more than fast enough to compensate the falloff in tunneling probability, and we obtain an infinite amount of tunneling through the barrier, coming from around $E = -\infty$.

That is clearly not right: We had better restrict quantum transition state theory, in the harmonic approximation, to temperatures well above $h\nu^*/2\pi k$. If the "vibrational energy" $h\nu^*$ is much above 500 cm^{-1}—as it usually is when the motion along the reaction coordinate involves transfer of a light atom such as hydrogen[20,21]—quantum transition state theory in the harmonic approximation cannot be used at room temperature.

This is distressing, because we wanted a low-temperature theory. Quantum transition state theory in the harmonic approximation will not work at low

temperatures, for the tunneling is wrong, and will not work at high temperatures, for the harmonic approximation is wrong.

We try to do better by using tunneling corrections calculated from a one-dimensional barrier of more reasonable shape. First we have to choose the barrier.

The harmonic approximation is a one-parameter fit to the actual potential; we should do better with a two-parameter fit, so we "stick" an Eckart potential[22] on the saddle point, because the solution of the Schrödinger equation is known for this potential, and play with the parameters until the fit looks good.

But that seems a bit arbitrary, so next we extend the reaction normal coordinate out in a straight line from the saddle point and examine how the actual potential varies along it. We find that after falling for a while the potential turns around and shoots up, as two atoms squash together (see Fig. 4). That was a mistake.

Maybe we should look at the potential as a function of distance along the reaction path leading from saddle point to reactants and products. Now the barrier has a reasonable shape, but what is the effective mass in a one-dimensional barrier penetration calculation?

Therefore we use the normal coordinates defined by the saddle point and mass-weight them; now the motion of the system is that of a single particle of definite mass in $3N$ dimensions, but we have to reexpress the potential in these coordinates and calculate a new reaction path. The curve of steepest descent from the saddle point will be different in mass-weighted coordinates.

Then it occurs to us, for physical reasons, that the height of the barrier to be surmounted ought to be the activation energy for the reaction. This is not the distance from reactant minimum to saddle point, but evidently—from Eq. (41)—the distance from zero-point energy of the reactants to zero-point energy of the transition state, so at every point along the reaction path in mass-weighted coordinates we add in the zero-point energy of vibration normal to the reaction path. That seems logical, because what we must be thinking—when we calculate tunneling through a one-dimensional barrier defined by the reaction path—is that the dynamical problem is in some sense approximately separable, so the vibrations normal to the reaction path are independent of motion along the path, the system maintains the vibrational quantum numbers with which it started, and the energy left to motion along the reaction path is total energy less potential energy less the vibrational energy of the state.

Well, actually, maybe we should do this vibrationally adiabatic tunneling correction separately for each vibrational state.

But now there is another problem. Even if the energy were constant along the reaction path—no barrier—the reaction path would still, in general, curve in $3N$-dimensional space, and if we shoot a particle down a curved trough, it

will not all come out the other end. Curvature of the reaction path must also affect tunneling. Possibly we should displace the reaction path until centrifugal force balances the potential force normal to the reaction path.[23,24]

We have chosen a potential, somehow; we now solve the one-dimensional Schrödinger equation at many energies and calculate the thermal average,

$$\int dE\, P(E) \exp(-E/kT) \tag{47}$$

To interpret the result we ask what energies contribute most to the integral. We calculate the position of the maximum of the integrand. If $h\nu^*/kT$ is substantially less than 2π, where ν^* is the frequency associated with the top of our barrier, the maximum of the integrand is around $E = 0$ relative to the barrier top, and we have essentially the harmonic approximation. If $h\nu^*/kT$ is substantially greater than 2π, however, we find the maximum around the energy at which $h\nu(|E|)/kT = 2\pi$, where $\nu(|E|)$ is the classical frequency of motion at energy $|E|$ in the well formed by turning the barrier upside down [to see this, use the semiclassical barrier penetration formula for $P(E)$[25]]. Because $\nu(|E|)$ should decrease as E goes down ($|E|$ goes up), because the effective barrier to reaction should open out—relative to an inverted parabola—as we move away from the saddle point, the reaction rate is dominated by tunneling at lower and lower energy as temperature decreases. At low temperatures most of the reaction rate is tunneling through a very thick region extending far from the saddle point.

In the rate formula, then, should we still be using partition functions evaluated right at the saddle point, as if the saddle point were still dominant?

One begins to appreciate that quantum transition state theory is not so well founded as its classical counterpart.

For a clear discussion of the definition of various one-dimensional tunneling corrections, and of their respective merits as judged by comparison with exact quantum calculations for the collinear $H + H_2$ reaction, the reader should consult an important series of articles by Truhlar, Kuppermann, and Adams.[26-29] We shall not pursue the subject further; instead we shall outline, in Section 3.2, two recent attempts at a quantum transition state theory that go beyond the separable approximation and proceed by close analogy with the classical variational formulation.

3.2. Beyond the Separable Approximation

We need first a quantum formula for the equilibrium rate of the reaction $A + B \rightarrow C + D$ analogous to the classical flux integral expression. It is derived as in the classical theory: We insist that reactants be maintained at equilibrium, look for the steady state density operator arising from this equilibrium distribution, and calculate the steady state rate of product formation as the flux, across

a surface separating reactant and product, associated with this density. The appropriate density operator is $P \exp(-H/kT)$, where P projects onto states that in the indefinite past were pure reactant, that is, $P\psi = \psi$ if the wave function $\exp(-iHt/\hbar)\psi$ describes pure $A + B$ as $t \to -\infty$ and $P\psi = 0$ if the wave function $\exp(-iHt/\hbar)\psi$ has no $A + B$ component as $t \to -\infty$. The density function in configuration space defined by this operator is $\rho(\mathbf{q}) = \langle \mathbf{q}|P \exp(-H/kT)|\mathbf{q}\rangle$, and the flux vector at $\mathbf{q}$ associated with this density is obtained in standard fashion by casting Schrödinger's equation into the form of a continuity equation for $\rho(\mathbf{q})$.

We shall illustrate with one-dimensional model of Section 2.2 to fix the ideas. The rate of barrier passage is proportional to

$$h^{-1} \int_0^\infty dp \frac{p}{m} P(p) \exp\left(-\frac{p^2}{2mkT}\right) \tag{48}$$

where $P(p)$ is the quantum probability that a particle, incident from the left with momentum p, crosses the barrier [the classical limit of Eq. (48) is $(kT/h)\exp(-E^{\ddagger}/kT)$].† The relevant solution of the Schrödinger equation is denoted $|p^+\rangle$, with asymptotic behavior

$$\langle q|p^+\rangle = \begin{cases} e^{ipq/\hbar} + R(p)e^{-ipq/\hbar}, & q \to -\infty \\ T(p)e^{ip'q/\hbar}, & q \to +\infty \end{cases} \tag{49}$$

where p' is the "product" momentum determined by conservation of energy, $R(p)$ and $T(p)$ are reflection and transmission coefficients, and the superscript $+$ on $|p^+\rangle$ is self-explanatory to anyone familiar with the standard confusing notation of scattering theory. The probability of crossing the barrier is§

$$P(p) = (p'/p)|T(p)|^2 \tag{50}$$

For the rate of barrier passage we can therefore write

$$h^{-1} \int_0^\infty dp \frac{p'}{m} |T(p)|^2 \exp\left(-\frac{p^2}{2mkT}\right) \tag{51}$$

Now consider the one-dimensional flux operator $j(q)$, defined by its matrix elements:

$$\langle \phi|j(q)|\psi\rangle = (-i\hbar/2m)(\phi^*\psi' - \phi^{*'}\psi)(q) \tag{52}$$

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†There are a lot of p's in this chapter, both capital and lowercase; we hope that the reader does not confuse $P(p)$ with the projection operator P or with the permutations P of Section 2.4.

§Not just $|T(p)|^2$. Think of sending a long wave packet ψ of well-defined momentum p against the barrier. The probability that it gets across is the integral of $|\psi|^2$ on the right after collision with the barrier, divided by the integral of $|\psi|^2$ on the left before collision with the barrier. If the incident packet takes, say, an hour to cross a fixed point to the left, the transmitted packet will take an hour to cross a fixed point to the right. But on the right the particle is traveling with momentum p', on the left with momentum p, so the transmitted packet is p'/p as long as the incident packet.

where $\psi' = d\psi/dq$, etc. If q lies far to the right of the barrier, we have [from Eq. (49)]

$$\langle p^+|j(q)|p^+\rangle = (p'/m)|T(p)|^2 \tag{53}$$

But in fact $\langle p^+|j(q)|p^+\rangle$ is independent of q (by direct computation, using the fact that $|p^+\rangle$ satisfies the Schrödinger equation). Therefore the rate is proportional to

$$h^{-1} \int_0^\infty dp \langle p^+|j(q)|p^+\rangle \exp\left(-\frac{p^2}{2mkT}\right) \tag{54}$$

evaluated at any q.

We need some elements of the formal theory of scattering, specialized to one dimension. First we define the scattering states $|p^+\rangle$ for negative p: $|p^+\rangle$ is the solution of Schrödinger's equation with asymptotic behavior

$$\langle q|p^+\rangle = \begin{cases} e^{ipq/\hbar} + R(p)e^{-ipq/\hbar}, & q \to +\infty \\ T(p)e^{ip'q/\hbar}, & q \to -\infty \end{cases} \tag{55}$$

where p' is again determined by conservation of energy. The states $|p^+\rangle$ are eigenfunctions of the Hamiltonian,

$$H|p^+\rangle = (p^2/2m)|p^+\rangle \tag{56}$$

and if the potential has no bound states, they are complete, so that a state $|\psi\rangle_t$ evolving in time under the Hamiltonian H can be expanded in the $|p^+\rangle$,

$$|\psi\rangle_t = h^{-1} \int dp\, a(p)e^{-ip^2t/2m\hbar}|p^+\rangle \tag{57}$$

Let $|p\rangle$ denote the plane waves,

$$\langle q|p\rangle = e^{ipq/\hbar}, \qquad \text{all } q \tag{58}$$

$|p^+\rangle$ "evolves" from $|p\rangle$ in the sense that, as $t \to -\infty$, $|\psi\rangle_t$ is indistinguishable from the state

$$h^{-1} \int dp\, a(p)e^{-ip^2t/2m\hbar}|p\rangle \tag{59}$$

The normalization of the scattering states is therefore identical to that of the plane waves,

$$\langle p'^+|p^+\rangle = \langle p'|p\rangle = h\delta(p'-p) \tag{60}$$

and we can calculate the expansion coefficients of any state $|\psi\rangle$:

$$|\psi\rangle = h^{-1} \int dp|p^+\rangle\langle p^+|\psi\rangle \tag{61}$$

We define a projector P by

$$P|\psi\rangle = h^{-1} \int_0^\infty dp|p^+\rangle\langle p^+|\psi\rangle \tag{62}$$

From Eq. (59) we deduce that if $P|\psi\rangle_t = |\psi\rangle_t$, then $|\psi\rangle_t$ is pure reactant in the indefinite past; if $P|\psi\rangle_t = 0$, then $|\psi\rangle_t$ is pure product in the indefinite past. P projects onto the subspace of states arising from pure reactant. We may write

$$P = h^{-1} \int_0^\infty dp |p^+\rangle\langle p^+| \tag{63}$$

and if O is any operator, we have

$$\text{Tr } OP = h^{-1} \int_0^\infty dp \langle p^+|O|p^+\rangle \tag{64}$$

In particular, the rate (54) can be written as

$$\text{Tr } j(q)Pe^{-H/kT} \tag{65}$$

that is, as the flux through q associated with the partial equilibrium density operator $P \exp(-H/kT)$ arising from reactants in equilibrium.

For the two-dimensional problem of Section 2.3—a particle of unit mass moving on the plane in a potential $V(\mathbf{q})$—the quantum rate is proportional to the flux integral

$$\int ds \, \mathbf{n}_s \cdot \text{Tr}[\mathbf{j}(\mathbf{q}_s)Pe^{-H/kT}] \tag{66}$$

where $\mathbf{q}_s$ is a curve separating reactants from products, $\mathbf{j}(\mathbf{q})$ is the two-dimensional flux operator with matrix elements

$$\langle\phi|\mathbf{j}(\mathbf{q})|\psi\rangle = (-i\hbar/2)[\phi^*(\nabla\psi) - (\nabla\phi)^*\psi](\mathbf{q}) \tag{67}$$

and P projects onto the subspace of states arising from pure reactant. As in the one-dimensional case, we can construct P from scattering states of the Schrödinger equation that "evolve" out of pure reactant states, that is, states that are products of a reactant vibrational state and a plane wave headed toward the region of interaction.

There is one difference between Eq. (66) and the classical formula (17), important in theory but not usually in practice: A state evolving from pure reactant may—if total energy permits—have amplitude for dissociation to free particles as well as amplitude for reaction. In classical theory this is no problem: We simply focus on the trajectories we want, the reactive trajectories, ignoring all trajectories that lead to dissociation or back to reactant. In quantum theory this is not possible: We cannot break P into a sum of two projectors, one describing reaction and one describing nonreaction and each commuting with the Hamiltonian. We can require of a solution of Schrödinger's equation that it describe pure reactant in the indefinite past or pure product in the indefinite future; we cannot require both. The curve $\mathbf{q}_s$ must therefore be chosen so that Eq. (66) includes no contribution from dissociation, that is, $\mathbf{q}_s$ must "hug" the asymptotic product region in such a way that, at infinite separation of product,

no part of the asymptotic free-atom region of the plane lies to the product side of $\mathbf{q}_s$.

So much for preamble. The transition state approximations suggested by this formulation of quantum rate theory are simply described.

McLafferty and Pechukas[30] looked for an upper bound to the quantum flux, because classical transition state theory provides an upper bound to the classical rate constant. We can reach classical transition state theory from the exact classical flux expression in two stages: First, we cast out the contribution from phase points on the transition state that are reactive but have momentum pointing the wrong way (i.e., back toward reactant); second, we add in the contribution from phase points that are nonreactive but have momentum pointing the right way (i.e., toward product). To see how this goes in quantum theory, look at the one-dimensional flux

$$\mathrm{Tr}\, j(q) P e^{-H/kT} \tag{68}$$

$j(q)$ is a Hermitian operator; we break it into positive and negative parts,

$$j(q) = j_+(q) + j_-(q) \tag{69}$$

where j_+ is obtained from j by setting all negative eigenvalues to zero and j_- by setting all positive eigenvalues to zero. Because the average of a negative operator cannot be positive, we have

$$\mathrm{Tr}\, j(q) P e^{-H/kT} \leqslant \mathrm{Tr}\, j_+(q) P e^{-H/kT} \tag{70}$$

This is the quantum analogue of casting out reactive phase points with negative momentum. Now let Q be the projector orthogonal to P, $P + Q = I$, $PQ = 0$. The average of the positive operator j_+ over the density $Q\,\exp(-H/kT)$ cannot be negative, so

$$\mathrm{Tr}\, j_+(q) P e^{-H/kT} \leqslant \mathrm{Tr}\, j_+(q) e^{-H/kT} \tag{71}$$

and we have the quantum analogue of adding in nonreactive phase points with positive momentum. Quantum transition state theory, then should read

$$\mathrm{Tr}\, j(q) P e^{-H/kT} \leqslant \mathrm{Tr}\, j_+(q) e^{-H/kT} \tag{72}$$

with interpretation as in classical theory: Transition state theory replaces the exact reactive flux through the transition state with the thermally averaged flux in the product direction.

The right-hand side of inequality (72) is indeed an upper bound to the quantum rate, but it is not one to write home about: It is always infinity. The problem is with the quantum current operator $j(q)$. This is a highly singular operator, as one would guess from the fact that its matrix element between any two wave functions depends only on the behavior of the wave functions in an infinitesimal neighborhood of q. To make progress it is necessary to "average"

the current operator. If $f(q)$ is any positive function, normalized so that

$$\int dp\, f(q) = 1 \tag{73}$$

we can write the exact flux integral equally well as

$$\int dp\, f(q)\, \mathrm{Tr}\, j(q) P e^{-H/kT} \tag{74}$$

and finite upper bounds to Eq. (74) can be derived along the lines of inequalities (70) and (71). This quantum transition state theory, then, involves a transition state with a certain width, defined by the weighting function f, and we are instructed to vary f so as to minimize the transition state rate. The theory can be easily generalized to more than one dimension without invoking separability.

The trouble is that the results are lousy: For the infinite parabolic barrier in one dimension McLafferty and Pechukas found that at all temperatures the best transition state rate overestimates the true rate of barrier passage by an even greater factor than the classical kT/h underestimates the rate. Therefore one cannot look here for a solution to the low-temperature tunneling problem of transition state theory, and there are strong arguments of a physical nature that any transition state upper bound to the quantum rate must be similarly inaccurate.

Once one gives up the idea of bounding the quantum rate, the possibilities for a quantum transition state theory are endless: Any expression that reduces to the classical result in the limit $h \to 0$ is a possible transition state theory. A good theory is one that is easy to work with and that holds out the promise of accurate results. On both counts Miller's recent suggestion[31] seems inspired.

In essence Miller proposes that we use the flux integral rate expression of *classical* transition state theory and simply replace the classical Maxwell–Boltzmann factor $\exp(-H/kT)$ with the phase space function generated from the quantum operator $\exp(-H/kT)$ by Wigner's prescription[32]; in one dimension,

$$h^{-1}\exp[-H(p, q)/kT] \to h^{-1}\int dq'\, e^{ipq'/\hbar}\langle q - q'/2|e^{-H/kT}|q + q'/2\rangle \tag{75}$$

One comes to this theory from the quantum expression (65) by replacing the dynamic projector P with the projector P_+ onto plane waves of positive momentum,

$$P_+ = h^{-1}\int_0^\infty dp\, |p\rangle\langle p| \tag{76}$$

the quantum analogue of replacing χ_r by χ_+ (Section 2.2). However, the quantum rate is not unambiguously defined by this replacement; we have

$$\mathrm{Tr}\, j(q) P e^{-H/kT} = \mathrm{Tr}\, j(q) e^{-H/kT} P \tag{77}$$

because P commutes with H, but

$$\text{Tr } j(q)P_+e^{-H/kT} \neq \text{Tr } j(q)e^{-H/kT}P_+ \tag{78}$$

because P_+ does not commute with H or with j. Miller defines the rate by interpreting $j(q)P_+$ as the operator associated by Weyl correspondence to the flux factor in the analogous classical expression; this definition is mathematically equivalent to using the classical flux factor in combination with the Wigner function associated to $\exp(-H/kT)$.

Miller's rate expression has many virtues. First, it passes the elementary test of getting right the rate for passage over an infinite parabolic barrier, and furthermore the classical phase space integral of the Wigner function associated to the quantum operator $\exp(-H/kT)$ gives the correct quantum partition function, so we are guaranteed that in the saddle point harmonic approximation we shall obtain the transition state rate of the previous section, correct in both the tunneling correction along the reaction coordinate and in the partition function for vibrations perpendicular to the reaction coordinate. Second, the Wigner function is well adapted to semiclassical approximation. This is important for the very low-temperature region where tunneling dominates the reaction rate and the semiclassical theory of multidimensional tunneling (also due to Miller[33]) should be accurate. Miller has in fact given a beautiful analysis of the semiclassical limit of his rate expression,[34] and we should soon have results on the $H + H_2$ collinear reaction to compare with accurate quantum calculations and with the various one-dimensional tunneling corrections mentioned in the preceding section. These calculations will indicate whether the Wigner function substitution should be regarded as the definitive version of quantum transition state theory or whether the problem is still unsettled.

The reader may be—in fact, should be—exasperated with all this uncertainty about what quantum transition state theory ought to be when tunneling dominates the rate. He will point out that what we need, after all, is just a simple dynamical theory of reactive cross sections near threshold. Look at the problem in the exothermic direction; we have only to follow a few low-energy reactant pairs as they tunnel through to become product in order to have a decent picture of threshold behavior. However, each wave function, when it reaches the product region, will divide into many branches, for the reaction is exothermic and many final states are accessible. In a simple theory we do not want to follow all the rivulets of the wave function, so we want to get reaction cross sections out of the wave while it is still "simple"—that is, before it gets to the product region. The only way to do it is by calculating the flux of the wave across some surface in the tunneling region, so we want a simple dynamical theory of the flux.

Go to it; when you find it, *that* will be quantum transition state theory.

4. Transition State Theory of Complex Reactions

4.1. Rates of Complex Formation and Decay

Again we shall consider a bimolecular reaction proceeding through an intermediate, $A + B \rightleftharpoons * \rightleftharpoons C + D$, but now we suppose that $*$ is a long-lived collision complex as produced, for example, by a deep hole in the potential surface between reactants and products. We imagine that a reactant pair $A + B$ or product pair $C + D$ enters the complex region and is subjected to strong forces and violent motion and quickly forgets its origins as $A + B$ or $C + D$. The complex may eventually break up to $A + B$—we shall call this possibility 1—or to $C + D$—possibility 2. It is the essence of the statistical theory of reactions proceeding through a complex that we assume that the probabilities P_1 and P_2 for the two modes of breakup are independent of how the complex is formed.[†]

The point of view here is exactly opposite that of transition state theory of direct reactions. There, we assume that at the transition state we can distinguish absolutely between trajectories coming from reactant $A + B$ and trajectories coming from product $C + D$ by looking at the direction of motion along the reaction coordinate; here, we assume that in the complex we absolutely cannot distinguish between trajectories from reactants and trajectories from products.

At equilibrium the rate at which complex is formed from $A + B$ is equal to the rate at which complex breaks up to $A + B$, and similarly the rate of complex formation from $C + D$ is balanced by the rate of breakup to $C + D$. If $k_1[A][B]$ is the rate of complex formation from reactants and $k_2[C][D]$ the rate from products, we must have

$$k_1[A][B] = P_1(k_1[A][B] + k_2[C][D])$$
$$k_2[C][D] = P_2(k_1[A][B] + k_2[C][D]) \tag{79}$$

Suppose that to form a complex reactants must pass through transition state 1, whereas products must go through transition state 2, that is, the complex region is separated on either side from reactants and products by a transition state, and the theory of Section 2 can be used to calculate the rate constants k_1 and k_2. Then

$$k_1 = (kT/h)(Q_1^{\ddagger}/Q_A Q_B), \qquad k_2 = (kT/h)(Q_2^{\ddagger}/Q_C Q_D) \tag{80}$$

and because

$$[A][B]/Q_A Q_B = [C][D]/Q_C Q_D \tag{81}$$

we have

$$P_1 = Q_1^{\ddagger}/(Q_1^{\ddagger} + Q_2^{\ddagger}), \qquad P_2 = Q_2^{\ddagger}/(Q_1^{\ddagger} + Q_2^{\ddagger}) \tag{82}$$

[†]The theory of this section is in essence just the theory of unimolecular reactions (see Chapter 3) applied to bimolecular reactions. Keck first gave the transition state formulation of the theory for bimolecular reactions[35]; see also the 1965 articles by Nikitin.[36,37]

The probability that the system leaves the complex region through a given exit is proportional to the width of the exit, as measured by its partition function.

P_1 and P_2 define "branching ratios" for breakup of the complex, that is, relative rates for the possible modes of decomposition. From transition state theory we can calculate as well the absolute rate constants for breakup of the complex. At equilibrium the concentration of complexes is proportional to the partition function per unit volume, Q^*, associated with the complex region of phase space:

$$[*] = Q^*[A][B]/Q_A Q_B = Q^*[C][D]/Q_C Q_D \tag{83}$$

The rate at which complex breaks up to, say, $C+D$ is equal to the rate of formation of complex from $C+D$,

$$k_2[C][D] = (kT/h)Q_2^{\ddagger}[C][D]/Q_C Q_D = (kT/h)Q_2^{\ddagger}[*]/Q^* \tag{84}$$

so the rate constant for breakup of complex to $C+D$ is

$$(kT/h)Q_2^{\ddagger}/Q^* \tag{85}$$

But we have made an error. A particular complex will of course have a definite energy, and the probabilities P_1 and P_2 will in general depend on energy. If the energy is too low, for example, it may be impossible for a complex formed from $A+B$ to decompose to give $C+D$. We should use microcanonical transition state theory (see Section 2.3) and calculate branching ratios for complex breakup as a function of energy.

The branching ratios will depend only on internal energy of the complex, not on the motion of the center of mass, and the same is true of the energy-dependent rate constants for complex formation from reactants and products. For example, at transition state 1 the Hamiltonian is

$$H = \mathbf{P}^2/2M + p_1^2/2m_1^* + h(\gamma_1) \tag{86}$$

where $\mathbf{P}$ is center of mass momentum, M is total mass, p_1 is the momentum along the reaction coordinate, m_1^* is the associated mass, and $h(\gamma_1)$ is the internal energy of the transition state as a function of the remaining $3N-4$ coordinates and $3N-4$ momenta of the N-particle system, collectively denoted γ_1. For the rate of complex formation through transition state 1 we can write

$$\frac{kT}{h}Q_1^{\ddagger} = \frac{1}{h^{3N}} \int_0^{\infty} dp_1 \int d\mathbf{P} \int d\gamma_1 \frac{p_1}{m_1^*} \exp\left(-\frac{H}{kT}\right)$$

$$= \frac{1}{h^3} \int d\mathbf{P} \exp\left(-\frac{\mathbf{P}^2}{2MkT}\right) \int dE\, k_1(E) \exp\left(-\frac{E}{kT}\right) \tag{87}$$

where

$$k_1(E) = \frac{1}{h^{3N-3}} \int_0^\infty dp_1 \int d\gamma_1 \frac{p_1}{m_1^*} \delta\left(E - \frac{p_1^2}{2m_1^*} - h(\gamma_1)\right)$$

$$= \frac{1}{h^{3N-3}} \int_0^\infty dE' \int d\gamma_1 \delta(E - E' - h(\gamma_1))$$

$$= \frac{1}{h^{3N-3}} \int_{h(\gamma_1)\le E} d\gamma_1$$

$$= \frac{N_1^\ddagger(E)}{h} \tag{88}$$

Here $N_1^\ddagger(E)$ is the "volume" $\int d\gamma_1$ of the transition state phase space up to energy E, divided by h^{3N-4}, that is, the semiclassical approximation to the number of internal quantum states at transition state 1 with energy $\le E$. Clearly, the only alteration necessary for a quantum theory of complex breakup is replacement of $N_1^\ddagger(E)$ by the correct quantum count of states.

At equilibrium, flux into the complex region of phase space through transition state 1 will be balanced, at every energy, by flux out, so we have

$$k_1(E) = P_1(E)[k_1(E) + k_2(E)] \tag{89}$$

and therefore

$$P_1(E) = N_1^\ddagger(E)/[N_1^\ddagger(E) + N_2^\ddagger(E)] \tag{90}$$

The lifetime of the complex will also depend on energy. Because

$$Q^* = (1/h^{3N}) \int d\Gamma \exp(-H/kT)$$
$$= (1/h^3) \int d\mathbf{P} \exp(-\mathbf{P}^2/2MkT) \int dE\, N(E) \exp(-E/kT) \tag{91}$$

where the integrals are over the region of phase space defining the complex and $N(E)$ is the density of internal states of the complex (number of states per unit energy), the rate constant for breakup through transition state 1 of complexes with energy in range dE around E is

$$\underset{\text{?}}{} \quad k_1(E)\, dE/N(E)\, dE = (1/h)N_1^\ddagger(E)/N(E) \tag{92}$$

$N_1^\ddagger$ is dimensionless, the units of $N(E)$ are energy^{-1}, so the units of Eq. (92) are time^{-1}, as they should be.

Further refinement is possible: A given complex has definite angular momentum about the center of mass, and the branching ratios and lifetimes of the complex will in general depend on both energy and angular momentum. We shall put off this discussion until Section 4.3. In Section 4.2 we shall discuss the dynamical foundations of the theory.

$dN = N(E)dE = \#\ of\ states\ in\ complex...$

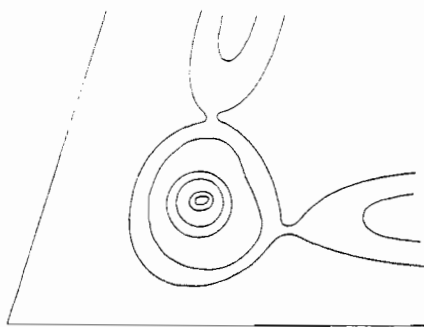$\dfrac{k_1^\ddagger dE}{dN}$

$...$ pechukas

Fig. 9. Two-dimensional model for transition
state theory of complex reactions.

4.2. Dynamical Foundations

The dynamical justification of statistical theory for complex reactions, crudely stated, is that a trajectory falling into a deep potential well will execute a motion so complicated, and so unstable with respect to its initial conditions, that "on average" the behavior of the trajectory will be characteristic of the entire region of phase space defining the complex, independent of the point of entry into this region.

It is an interesting but difficult problem to make this argument more precise.* We suspect that statistical behavior, and the branching ratios calculated in Section 4.1, must follow if the complex is sufficiently long-lived (that is, if the exits from the complex are sufficiently narrow), but we know of no demonstration that this is in fact the case. Statistical theory for complex reactions is less secure, in its dynamical foundations, than transition state theory of direct reactions.†

The problems one encounters in analyzing the dynamics of complex formation and decay can already be seen in the simplest model, motion of a unit mass in two dimensions [there is no (classical) one-dimensional model for complex formation] under the influence of a potential with a deep well separating region 1 from region 2 and "protected" on either side by transition states (Fig. 9). We shall consider trajectories of fixed energy E and assume that outside the region of the well the potential is such that a particle leaving the complex region through either transition state will never return. No trajectory, then, can "visit" the complex region more than once in its history.

Let $\chi_1(\mathbf{p}, \mathbf{q})$ be the characteristic function of phase points lying on trajectories that in the indefinite past are in region 1 and that enter the complex region at some time in their history; $\chi_2(\mathbf{p}, \mathbf{q})$, similarly, is the characteristic

*Computer "experiments" are therefore most informative; see the trajectory calculations of Brumer and Karplus on alkali halide exchange reactions.[38]
†On the other hand, transition state theory of complex reactions may give accurate results, by accident, which transition state theory of direct reactions never can: When it fails, the latter always fails to the high side of the true reaction rate.

function of phase points lying on trajectories that enter the complex from region 2. So that a trajectory of energy E will be reactive—that is, get from region 1 to region 2—the trajectory must pass through the complex region, and the rate of reaction $k_{12}(E)$ is the flux associated with χ_1 across any curve separating regions 1 and 2 [nonreactive trajectories—trajectories that enter the complex from region 1 and exit back to region 1—contribute to χ_1 but not to the flux associated with χ_1 (see Sections 2.2 and 2.3)]. Therefore, in the notation of Section 2.2,

$$k_{12}(E) = \int d\mathbf{p} \, ds(\mathbf{p} \cdot \mathbf{n}_s)\chi_1(\mathbf{p}, \mathbf{q}_s)\delta(E - H(\mathbf{p}, \mathbf{q}_s)) \tag{93}$$

The total rate of formation of complex, from region 1, is the rate at which trajectories from region 1 cross transition state 1 *into the complex region*; that is, again in the notation of Section 2.2,

$$k_1(E) = \int d\mathbf{p} \, ds(\mathbf{p} \cdot \mathbf{n}_s)\chi_1(\mathbf{p}, \mathbf{q}_s)\chi_+(\mathbf{p}, \mathbf{q}_s, \mathbf{n}_s)\delta(E - H(\mathbf{p}, \mathbf{q}_s)) \tag{94}$$

where the integral is along transition state 1 and the unit normal $\mathbf{n}_s$ points to the complex region. By our assumption on the behavior of the potential outside the complex region, any trajectory that crosses transition state 1 into the complex must originate, in the indefinite past, from region 1, so $\chi_1\chi_+ \equiv \chi_+$ at the transition state, and $k_1(E)$ is just the rate of complex formation calculated by ordinary transition state theory of direct reactions.

Now $k_{12}(E) = k_1(E)P_{12}(E)$, where $P_{12}(E)$ is by definition the probability that a complex formed from region 1 will decay to region 2. The question is whether this probability is given correctly by the formula of the previous section,

$$P_{12}(E) = k_2(E)/[k_1(E) + k_2(E)] \tag{95}$$

where $k_2(E)$ is the rate of complex formation from region 2, calculated as in Eq. (94) by ordinary transition state theory of direct reactions at transition state 2.

It is presumably the random and irregular motion inside the complex that leads to statistical behavior, so we want to examine the functions χ_1 and χ_2 inside the complex region. First, we ask whether the entire set of states of the complex is accessible, either to reactant or to product, that is, does $\chi_1 + \chi_2 = 1$ at every point in the complex region for which $H(\mathbf{p}, \mathbf{q}) = E$? The answer in general is no; a phase point $(\mathbf{p}, \mathbf{q})$ in the complex region is accessible from outside only if the trajectory through it manages eventually to escape the complex. There may be classical trajectories that never leave the complex, although energy permits, because they never get close to either of the transition states. In the theory of unimolecular reactions one speaks of "inactive modes" that are insulated from the rest of the molecule for times comparable to the lifetime of the molecule, with complete energy sharing only among the remaining modes, but classical–mechanical reality may be more complicated: Rather than dividing into "active" and "inactive" modes, the classical motion

may be such that some of the trajectories on the energy surface are "irregular" and wander all over the surface while the rest are "regular" and confined forever to a corner of the surface (see the excellent review by Ford[39]). Intuition and computer calculations agree that irregular motion dominates if the potential well is deep, and in any case *quantum* bound states at energies above dissociation are rare—the "tail" of the wave function extends over all space, in particular out the exits from the complex, and sooner or later the wave function is pulled out of the complex by its tail. But this may take a while, and the rate of decomposition of the complex can be greater than that calculated by Eq. (92) if the density of states in effective communication with the outside is reduced by the occurrence of long-lived quasi-bound states.

So be it; for bimolecular reactions we need only the branching ratios, not the absolute rate of decomposition of the complex, and we can calculate probabilities with respect to the distribution that actually obtains on the energy surface, determined by $\chi_1 + \chi_2$, rather than with respect to the full micro-canonical distribution. Let us calculate, for example, the probability that a complex, selected without regard to origin, decays to region 2. The trajectory through a phase point $(\mathbf{p}, \mathbf{q})$ leads to region 2 if and only if the time-reversed trajectory, through $(-\mathbf{p}, \mathbf{q})$, comes from region 2, so

$$P_2(E) = \frac{\int d\mathbf{p}\, d\mathbf{q} \chi_2(-\mathbf{p}, \mathbf{q}) \delta(E - H)}{\int d\mathbf{p}\, d\mathbf{q}[\chi_1(\mathbf{p}, \mathbf{q}) + \chi_2(\mathbf{p}, \mathbf{q})]\delta(E - H)} \tag{96}$$

where the integrals are over the region of phase space defining the complex. Because H is an even function of momentum, P_2 is also the probability that a complex, selected at random, comes from region 2.

Is $P_2(E)$ equal to $k_2(E)/[k_1(E) + k_2(E)]$, the probability that a complex will exit through transition state 2, irrespective of origin, as calculated by the flux integrals? Not necessarily; particles may enter the complex region at equal rates from sides 1 and 2, but if those from side 2 spend, on average, more time in the complex region than those from side 1, we shall find that $P_2(E)$ as calculated from Eq. (96)—the probability that a complex chosen at random comes from side 2—is greater than one half.

The moral is that probabilities calculated by phase space integration inside the complex region may not be the probabilities one needs for rate calculations. However, let us hope for the best; there is no reason to suspect a difference in lifetimes of complexes originating from the two sides, and that would in any case be out of keeping with the basic tenet of statistical theory, that complexes are essentially the same, no matter what their origin.

What we need, then, is $P_{12}(E)$, the probability that a complex originating from region 1 will decay to region 2,

$$P_{12}(E) = \frac{\int d\mathbf{p}\, d\mathbf{q} \chi_1(\mathbf{p}, \mathbf{q}) \chi_2(-\mathbf{p}, \mathbf{q}) \delta(E - H)}{\int d\mathbf{p}\, d\mathbf{q} \chi_1(\mathbf{p}, \mathbf{q}) \delta(E - H)} \tag{97}$$

and the question is whether Eq. (97) equals Eq. (96).

P_{12} is $\chi_2(-\mathbf{p}, \mathbf{q})$ averaged over the distribution χ_1, and P_2 is $\chi_2(-\mathbf{p}, \mathbf{q})$ averaged over the distribution $\chi_1 + \chi_2$. We see how the argument ought to go: If the motion inside the complex region is complicated and irregular, we expect that the distribution χ_1 will spread itself uniformly over the accessible region of the energy surface and be essentially indistinguishable from $\chi_1 + \chi_2$—not uniformly in the literal sense, of course; χ_1 is either one or zero, so it winds over the energy surface like the plague through Europe, missing some points while hitting their neighbors, and what we can expect is that the average of any *smooth* function over χ_1 should be identical to the average of that function over the full distribution $\chi_1 + \chi_2$.

There are two problems with this argument: First, it is not really correct, and second, if it were, it nevertheless would not apply to Eq. (97).

Calculate, for instance, the average momentum using each of the three distributions χ_1, χ_2, and $\chi_1 + \chi_2$. The averages all differ, because on balance points from region 1 are moving to region 2 and vice versa, whereas the average complex is going nowhere.

These differences in the averages of smooth functions are in fact small if the potential well is deep and χ_1 and χ_2 both cover a considerable part of the energy surface, but one still cannot infer that Eqs. (97) and (96) are equal: The function averaged over χ_1 in Eq. (97)—the function $\chi_2(-\mathbf{p}, \mathbf{q})$—is *not* a smooth function. If the motion of complexes arising from region 1 is complicated, so equally is the motion of complexes going to region 2, and Eq. (97) is in fact the overlap of two highly irregular functions. Simple analytical arguments about the magnitude of this overlap are suspect.

"Highly irregular functions" are perhaps not well correlated. What happens if we suppose that $\chi_1(\mathbf{p}, \mathbf{q})$ and $\chi_2(-\mathbf{p}, \mathbf{q})$ are uncorrelated with respect to the distribution $\chi_1 + \chi_2$? We obtain

$$
\begin{aligned}
P_{12} &= \frac{\int d\mathbf{p}\, d\mathbf{q}\chi_1(\mathbf{p}, \mathbf{q})\chi_2(-\mathbf{p}, \mathbf{q})\delta(E - H)}{\int d\mathbf{p}\, d\mathbf{q}\chi_1\delta(E - H)} \\[2mm]
&= \frac{\int d\mathbf{p}\, d\mathbf{q}\chi_1(\mathbf{p}, \mathbf{q})\chi_2(-\mathbf{p}, \mathbf{q})\delta(E - H)}{\int d\mathbf{p}\, d\mathbf{q}(\chi_1 + \chi_2)\delta(E - H)} \frac{\int d\mathbf{p}\, d\mathbf{q}(\chi_1 + \chi_2)\delta(E - H)}{\int d\mathbf{p}\, d\mathbf{q}\chi_1\delta(E - H)} \\[2mm]
&= \frac{\int d\mathbf{p}\, d\mathbf{q}\chi_1\delta(E - H)}{\int d\mathbf{p}\, d\mathbf{q}(\chi_1 + \chi_2)\delta(E - H)} \frac{\int d\mathbf{p}\, d\mathbf{q}\chi_2\delta(E - H)}{\int d\mathbf{p}\, d\mathbf{q}(\chi_1 + \chi_2)\delta(E - H)} \\[2mm]
&\quad \times \frac{\int d\mathbf{p}\, d\mathbf{q}(\chi_1 + \chi_2)\delta(E - H)}{\int d\mathbf{p}\, d\mathbf{q}\chi_1\delta(E - H)} \\[2mm]
&= P_1 \cdot P_2 \cdot \frac{1}{P_1} = P_2
\end{aligned}
\tag{98}
$$

Marvelous; we have restated, in obscure notation, the basic premise of statistical theory, that the future of a complex is uncorrelated with its past.

Statistical theory is easier to justify quantum mechanically, up to a point.[40] The properties of an isolated resonance—that is, a quasi-bound state with lifetime long compared to $h/\Delta E$, where ΔE is the distance in energy to the next resonance—are independent of the mode of formation: You cannot tell one uranium atom from another. If the resonance is *not* isolated, quantum theory encounters much the same difficulties as classical theory. Suppose, for instance, that ϕ_1 and ϕ_2 are neighboring quasi-bound states with energies E_1 and E_2 and that the system initially is in state $a_1\phi_1 + a_2\phi_2$; then

$$\begin{aligned}
\psi(t) &= a_1 e^{-iE_1 t/\hbar}\phi_1 + a_2 e^{-iE_2 t/\hbar}\phi_2 \\
&= e^{-iE_1 t/\hbar}(a_1\phi_1 + a_2 e^{-i\Delta Et/\hbar}\phi_2)
\end{aligned} \tag{99}$$

and the system will not "sample" all possible states, consistent with the absolute magnitudes $|a_1|$ and $|a_2|$, unless it lives for a time of order $h/\Delta E$.

In the statistical theory of complex formation and decay, we are dealing with isolated resonances when the lifetime of the complex is greater than $hN(E)$, where $N(E)$ is the density of states of the complex (that is, the inverse of the energy spacing between neighboring states). Because the lifetime of the complex is the inverse of the total rate constant for decay in all possible modes, from Eq. (92) we must have

$$\sum_i N_i^{\ddagger}(E) \simeq 1 \tag{100}$$

That is, statistical theory of complex decay is justified quantum mechanically when the exits from the complex are so narrow that no more than a few final states are possible. This makes sense: One state in, one state out, and therefore one state in the middle, and its properties must of course be independent of how it is formed. But the theory of isolated resonances rarely applies to molecular collisions, where the transition states leading to and from the complex region typically accommodate many states even at low energy.

In short, the dynamical foundations of statistical theory for complex reactions are not firmly settled. Nevertheless, physical intuition insists that the theory is correct. If a complex lives long enough, its dynamical state—either classical or quantum; it does not matter—will be an exceedingly sensitive function of initial state, and there is always in rate theory some averaging over initial state. It is not necessarily essential that statistical theory have a foundation in dynamics: The averaging over initial conditions may suffice. Consider, for example, a perfect spherical cavity, silvered on the inside, with a number of tiny holes to let light in and out; we shine a bulb for an instant behind one of the holes and photons start off in all directions around the cavity; the motion is perfect "regular"—there is no chance, in this case, that a photon trajectory "samples" all of phase space—yet the illumination leaking out any hole will certainly be proportional to the size of the hole, and any man who claims otherwise should be put away. Shouldn't he?

4.3. Loose Transition States and the Statistical Theory of Final State Distributions †

If the exit from a complex lies at large separation of the product molecules, where the interaction between them is weak or at any rate weakly dependent on their internal state, we have a "loose" transition state in which the product molecules vibrate and rotate freely. The counting of internal states at the exit [Eq. (88)] then has a significance beyond serving as a measure of the total rate of decay to product: These states are the possible final states of product, and the flux from complex to each of them is equal, so we can calculate the final state distributions arising from decay of the complex.

If the transition state entrance to the complex is also loose, we can calculate as well the rate of formation of complex from given internal states of the reactants. In keeping with the spirit of statistical theory we assume that decay of the complex is independent of its mode of formation, so we can determine state-to-state rates of reaction. If the transition states separating complex from reactants and products are loose, then, we should be able to calculate—within the statistical model—cross sections from given vibration–rotation states of reactants to vibration–rotation states of products.

How do loose transition states arise? A transition state is a surface of dynamical instability: Trajectories leaving to one side behave in a qualitatively different manner from those leaving to the other side. Suppose that we have two molecules with *no* potential barrier hindering approach but rather, at moderate to large distances, an attractive potential dependent to good approximation only on the distance r between the molecular centers of mass. There is a surface of dynamical instability here, even though the potential decreases smoothly toward small r: At given relative energy ε there is a distance r^* at which the two molecules will orbit about each other, each moving in a circle about the common center of mass. At this distance the attractive force between the molecules is just balanced by the centrifugal "force" driving them apart as they orbit each other. A trajectory of energy ε, starting at r^* and heading out, will escape to infinity; a trajectory of energy ε, starting at r^* and heading in, spirals to smaller and smaller r until the region of strong interaction is reached.

To determine r^* we look at the effective potential for radial motion in a central field,

$$V(r) + l^2/2\mu r^2 \tag{101}$$

where l is the orbital angular momentum and μ the reduced mass of the two molecules. If $V(r)$ is attractive and falls off faster than $1/r^2$ as $r \to \infty$, and if l is sufficiently small, this function will have a maximum at large r; call the position of the maximum $r^*(l)$. As l increases, $r^*(l)$ decreases until the maximum

†The statistical theory of final state distributions is due to Light and co-workers.[41–44] It is often called the *phase space* theory of chemical kinetics, because that is what Light named it.

disappears into a point of inflection where both the first and second derivatives of Eq. (101) vanish, or until the approximation of the intermolecular potential by a spherically symmetric function becomes untenable. The maximum is an "angular momentum barrier." A molecular pair with angular momentum l and relative energy of translation

$$\varepsilon = V(r^*) + l^2/2\mu r^{*2} \tag{102}$$

will not move off the top of the barrier once placed there: all the kinetic energy is in the angular direction, forever.

The orbiting parameters r, l, and ε are all interrelated: Any one determines the other two. In what follows the important variable is energy, so we define $r^*(\varepsilon)$ and $l^*(\varepsilon)$ as the orbiting distance and angular momentum at relative energy ε; $l^*(\varepsilon)$ is the maximum orbital angular momentum permitted to the complex at relative energy ε, for a colliding pair with greater angular momentum cannot reach the boundary of the complex at $r^*(\varepsilon)$.

This is clearly a model for reactions without activation energy. There is no potential barrier to formation of the complex, and in fact as the relative energy decreases, the size of the complex, as measured by its radius $r^*(\varepsilon)$, increases.

It is also possible to model reactions with activation energy by a potential permitting loose transition states. We simply put potential barriers in the entrance and exit channels, again dependent only on intermolecular separation.[†] To reach the complex region reactant molecules have to cross the barrier, so complex formation cannot take place at relative energy below the barrier maximum. At higher energies we get complex formation at any angular momentum low enough that the maximum in the effective potential (101) lies below the relative energy of translation. Again the transition state separation $r^*(\varepsilon)$ is determined by the maximum of Eq. (101), and the theory proceeds as indicated below.

As a model for reactions with activation energy this is very useful, because we obtain state-to-state cross sections, but not especially realistic. Reactions with appreciable activation energy usually have steric as well as energy requirements. If the reaction in fact proceeds through a complex, the entrance to the complex is generally well into the region where the potential depends strongly on relative orientation of the reactant molecules, and we have a "tight" transition state: The collision partners do not rotate and vibrate freely. Statistical theory can still be used to get state-to-state cross sections if the internal states at the entrance and exit to the complex correlate directly with vibration–rotation states of separated reactants and products, but this is an assumption about the dynamics outside the complex and not part of basic

†More generally, dependent on intermolecular separation and also on conserved dynamical properties of the separate molecules such as vibrational and rotational energy, to model collisions in which vibrational and rotational energy helps the colliding molecules surmount the barrier to reaction; see Reference 43.

statistical theory of complex formation and decay. We refer the reader to a recent stimulating article by Marcus for a theory of product energy distributions from tight transition states[45] and also to earlier articles by the same author for a discussion of final state distributions in the transition state theory of direct reactions.[46,47]

We shall now return to calculations on loose transitions states and look first at the rate of complex decay to, say, C+D. Each complex has definite energy and angular momentum, and the rate of complex decay to C+D will depend on the angular momentum of the complex as well as on energy, but for the moment we shall ignore that complication and calculate the full microcanonical rate $k(E)$.

The transition state is the set of all phase points with intermolecular separation $r^*(\varepsilon)$ and orbital angular momentum less than or equal to $l^*(\varepsilon)$, where ε is the relative translational energy of C+D. This is a rather complicated surface in phase space, and to calculate the flux through it in a straightforward fashion is a challenge; Eq. (88) is not directly applicable. Instead we use the fact that a system passing through the transition state, from the complex side out, inevitably becomes separated molecules, so we can calculate the flux just as well through a surface of fixed and large intermolecular separation r provided we restrict the integration to phase points that arise from complex decay.

At large r the interaction between C and D is negligible, and the Hamiltonian is

$$H = \mathbf{P}^2/2M + \mathbf{p}^2/2\mu + h_C(\gamma_C) + h_D(\gamma_D) \tag{103}$$

where $\mathbf{P}$ is center of mass momentum, M is total mass, $\mathbf{p}$ is the relative momentum of the two molecules, μ is the reduced mass, and $h_C(\gamma_C)$ and $h_D(\gamma_D)$ are the Hamiltonians of isolated molecules C and D as a function of "internal" phase points γ_C and γ_D [that is, γ_C is a point in the $(6N-6)$-dimensional phase space of coordinates and momentum relative to center of mass and total momentum of molecule C]. The microcanonical rate out of the complex at energy E is [see Eqs. (87) and (88)]

$$k(E) = \frac{1}{h^{3N-3}} \int \int d\gamma_C \, d\gamma_D \int d\mathbf{p} \int d\sigma \frac{\mathbf{p} \cdot \hat{\mathbf{r}}}{\mu} \chi(\mathbf{p}, \mathbf{r}, \gamma_C, \gamma_D)$$
$$\times \delta\left(E - \frac{\mathbf{p}^2}{2} - h_C(\gamma_C) - h_D(\gamma_D)\right) \tag{104}$$

where $d\sigma$ is an element of area on the sphere of radius r, $\hat{\mathbf{r}}$ is the unit vector in the outward radical direction, and χ is the characteristic function of phase points lying on trajectories that come from the complex. A phase point has come from the complex if the radial momentum $\mathbf{p} \cdot \hat{\mathbf{r}}$ is positive and the orbital angular momentum is less than $l^*(\varepsilon)$, where the relative translation energy ε is now simply $\mathbf{p}^2/2\mu$.

Fix **r** and do the integral over momentum first, using spherical polar coordinates with axis along $\hat{\mathbf{r}}$. The volume element is $p^2\,dp\,\sin\theta\,d\theta\,d\phi$, $\mathbf{p}\cdot\hat{\mathbf{r}}$ is $p\cos\theta$, and the angular momentum, in magnitude, is $rp\sin\theta$. The momentum integral is therefore

$$\int_{rp\sin\theta<l^*} d\mathbf{p}\frac{\mathbf{p}\cdot\hat{\mathbf{r}}}{\mu} = 2\pi\int dp\frac{p^3}{\mu}\int_0^{l^*/rp}\sin\theta\,d(\sin\theta)$$

$$= \int \pi\frac{l^{*2}}{r^2}\frac{p}{\mu}\,dp \equiv \int\pi\frac{[l^*(\varepsilon)]^2}{r^2}\,d\varepsilon \tag{105}$$

From the integral over the surface of the sphere we obtain a factor $4\pi r^2$, and therefore

$$k(E) = (1/h^{3N-3})\iiint d\gamma_C\,d\gamma_D\,d\varepsilon \cdot 4\pi^2 l^*(\varepsilon)^2\delta(E-\varepsilon-h_C(\gamma_C)-h_D(\gamma_D)) \tag{106}$$

$$\underbrace{}_{\varepsilon'}$$

which we can write in more suggestive form as

$$k(E) = h^{-1}\int dn(\varepsilon')N(E-\varepsilon') \tag{107}$$

using the functions
$$[E-\varepsilon \qquad \varepsilon' \quad \text{to get}\ (114)]$$

$$n(\varepsilon') = (1/h^{3N_C+3N_D-6})\iint_{h_C(\gamma_C)+h_D(\gamma_D)\le\varepsilon'} d\gamma_C\,d\gamma_D \tag{108a}$$

$$N(E-\varepsilon') = 4\pi^2 l^*(E-\varepsilon')^2/h^2 \tag{108b}$$

$n(\varepsilon')$ is the semiclassical approximant to the number of internal states of separated $C+D$ with total energy less than or equal to ε'. Going immediately to quantum mechanics, the analogue to Eq. (107) is therefore

$$k(E) = h^{-1}\sum_{i,j} N(E-E_C(i)-E_D(j)) \tag{109}$$

where i denotes a vibration–rotation state of C with energy $E_C(i)$, j denotes a vibration–rotation state of D with energy $E_D(j)$, and the sum is over all possible states of C and D with total energy less than E. The total rate $k(E)$ is the sum of rates to the various possible final states, and the rate to a given final state is

$$N(E-E_C(i)-E_D(j))/h \tag{110}$$

The essential feature of Eq. (110) is that the rate of complex decay to a given final state of separated $C+D$ depends only on the total energy of this state. Two quanta in a stretching vibration or 7 in a bending mode or 30 in rotation—it does not matter so long as the total energy is the same: Statistical theory predicts equal decay rate from the complex to each of these alternatives.

Relative decay rates to the possible final states of a given molecular pair are entirely determined, according to Eqs. (108b) and (110), by the behavior of the orbiting angular momentum $l^*(\varepsilon)$ as a function of energy. $l^*(\varepsilon)$ increases with relative energy ε (raise ε, and the effective potential at the maximum must increase, which can be arranged only by increasing l). At given total energy, therefore, the more energy one has in vibration–rotation of C and D, the less energy one has available to relative translation and the lower the rate of complex decay to the state in question. Statistical theory never predicts population inversion as a result of complex decay. In fact, if the total energy is large compared to the spacing of internal states of C and D, the low-lying states of the molecules are produced in a Maxwell–Boltzmann distribution,

$$N(E - E_C(i) - E_D(j))/N(E) = \exp\{-[E_C(i) + E_D(j)]/kT\} \qquad (111)$$

where the energies $E_C(i)$ and $E_D(j)$ in Eq. (111) are measured relative to the lowest vibration–rotation state of each molecule and T is determined "thermodynamically" by

$$T^{-1} = dS/dE \qquad (112)$$

where the "entropy" is

$$S = k \ln N(E) \qquad (113)$$

E is the maximum energy available to relative translation, that is, essentially the exothermicity if we are looking at products from a low-energy collision of unexcited molecules. If the potential $V(r)$ goes as $1/r^6$ at large distances (neutral products), $l^*(\varepsilon)$ goes as $\varepsilon^{1/3}$, and therefore the temperature is determined by $kT = 3E/2$; if $V(r)$ goes as $1/r^4$ at large distances (ion–molecule products), $l^*(\varepsilon)$ goes as $\varepsilon^{1/4}$, and the relation is $kT = 2E$.

The distribution of relative translational energy is determined by Eq. (107); we see that $P(\varepsilon)\,d\varepsilon$, the probability that translational energy lies in the range $d\varepsilon$ around ε, is proportional to

$$d\varepsilon N(\varepsilon)\rho(E - \varepsilon) \qquad (114)$$

where ρ is the density of internal product states. $N(\varepsilon)$ goes as $\varepsilon^{2/3}$ (neutral products) or $\varepsilon^{1/2}$ (ion–molecule products). If E is large compared to the level spacings of C and D and $\varepsilon \ll E$, we have

$$\rho(E - \varepsilon) \propto (E - \varepsilon)^n \propto \exp(-n\varepsilon/E) \qquad (115)$$

where the exponent n is one less than the power of T in the product of the classical vibration–rotation partition functions for the two molecules, because this product goes as

$$\int dE \rho(E) \exp(-E/kT) \propto \int dE E^n \exp(-E/kT) \propto T^{n+1} \qquad (116)$$

We get a T for each vibrational degree of freedom and $T^{1/2}$ for each rotational degree of freedom [see Eqs. (28) and (29)], and the reader can work out the various possibilities according to whether products are linear or nonlinear, atoms or molecules, and so on.

This translational energy distribution was derived by Safron et al. in $1972^{(48)}$ under the assumptions that the angular momentum of the complex is large compared to rotational angular momentum of reactants or products and that the lifetime of the complex is essentially independent of total angular momentum. Provided the orbital angular momentum of product at given relative energy ε is not limited to a value less than $l^*(\varepsilon)$ by the mode of formation of the complex, this is equivalent to using the full microcanonical rate $k(E)$ to calculate product distributions (see below).

We have been speaking of relative rates of complex decay to the possible final states of a particular arrangement channel (that is, fixed product molecules $C+D$). Relative rates to states of identical energy in different arrangement channels $(A+B, C+D, \text{etc.})$ are determined, in statistical theory, by the long-range forces and reduced masses in the various channels, for these are what determine $l^*(\varepsilon)$. Other things being equal, statistical theory favors products with high reduced mass and strong attractive interactions. As for the total decay rate to various channels, the more exothermic a given reaction, the more of that product we shall get (other things being equal): The greater the energy available for distribution among final states, the greater the number of final states available to accept that energy and the higher the total rate to the lot of them.

There is, however, a problem, at high energy, with the definition of the transition state as the maximum of the angular momentum barrier. If the relative energy of translation is too high, the position of the maximum, as determined by the long-range forces, moves into the region of the short-range forces.

We shall not pause to discuss the various possibilities for patching the theory in the very exothermic channels but instead shall consider now the role of angular momentum in statistical theory.

Ignoring the angular momentum of the complex can lead to serious errors. For instance, if the complex can be formed with at most 20 units of angular momentum from reactants but the complete energy surface of the complex "communicates" with states of product possessing up to 80 units of angular momentum, we shall probably be off by quite a bit in using the full microcanonical rate to product for calculating reaction cross sections. We need the probability of decomposition, to all possible final states, of a complex having definite energy E and definite angular momentum quantum numbers (J, M_J).

Look back at the full rate to $C+D$, Eq. (109). $N(\varepsilon)$ is the semiclassical approximant to the number of quantum states with orbital angular momentum

quantum number $L \leq l^*(\varepsilon)/\hbar$, because

$$N(\varepsilon) = \frac{4\pi^2 l^*(\varepsilon)^2}{h^2} = \frac{l^*(\varepsilon)^2}{\hbar^2} \simeq \sum_0^{l^*(\varepsilon)/\hbar} 2L+1 \tag{117}$$

We can therefore write

$$k(E) = h^{-1} \sum_{i,j} \sum_{L,M_L} 1 \tag{118}$$

where the sum over L is restricted to values less than $l^*(E - E_C(i) - E_D(j))/\hbar$.

Equation (118) says that the complex decays at equal rate to any of the possible final states (i, j, L, M_L) accessible from the complex. From these states we can construct linear combinations of definite (J, M_J); the total number of states will not change, and clearly statistical theory for decay of a complex of given (J, M_J) should require equal rate to each of the possible final states with these quantum numbers.

What we have, then, is just a counting problem in the addition of angular momentum, messy but straightforward, and the computer does it well. We are interested in the rate of production of product states lying in various subspaces labeled with quantum numbers (v_C, v_D, L_C, L_D, L), where v_C and v_D are vibrational quantum numbers, L_C and L_D rotational quantum numbers, and L the orbital angular momentum quantum number (if C or D is nonlinear, the third rotational quantum number is included in v_C or v_D). There are $(2L_C + 1)(2L_D + 1)(2L + 1)$ states in this subspace, and from then we can form a certain number of states with total angular momentum quantum numbers (J, M_J); let this number be $N(f, L | J, M_J)$, where f stands for the composite (v_C, v_D, L_C, L_D) specifying a vibration–rotation energy level of the product pair. We define

$$N(f|E, J, M_J) = \sum_{\hbar L < l^*(E - E_F)} N(f, L | J, M_J) \tag{119}$$

The rate of decay of complex with energy E and quantum numbers (J, M_J) to the vibration–rotation level f is proportional to $N(f|E, J, M_J)$; the probability that the complex decays to level f is therefore

$$P(f|E, J, M_J) = N(f|E, J, M_J) / \sum_f N(f|E, J, M_J) \tag{120}$$

where the sum in the denominator is over all accessible vibration–rotation levels of all possible molecular pairs arising from complex decay.

The cross section at total energy E from an initial state of reactant $A + B$ in vibration–rotation level i to vibration–rotation level f of product $C + D$, averaged over M_{L_A} and M_{L_B}, is

$$\sigma(f|i) = \sum_{J, M_J} P(f|E, J, M_J)\sigma(E, J, M_J|i) \tag{121}$$

where $\sigma(E, J, M_J|i)$ is the cross section for formation of complex with quantum numbers (E, J, M_J) from a state of i averaged over M_{L_A} and M_{L_B}. Two

molecules colliding with orbital angular momentum L' and relative momentum $\hbar k$ will contribute $^{(25)}$ $\pi(2L'+1)/k^2$ to the cross section for complex formation if $\hbar L'$ is less than $l^*(E - E_i)$ and zero otherwise. The probability that the pair gives a complex with quantum numbers (J, M_J) is

$$N(i, L'|J, M_J)/(2L'+1)(2L_A+1)(2L_B+1) \tag{122}$$

and so

$$\sigma(E, J, M_J|i) = \frac{\pi/k^2}{(2L_A+1)(2L_B+1)} \sum_{\hbar L' < l^*(E-E_i)} N(i, L'|J, M_J)$$

$$= \frac{\pi N(i|E, J, M_J)}{k^2(2L_A+1)(2L_B+1)} \tag{123}$$

The reaction cross section $\sigma(f|i)$, averaged over M_{L_A} and M_{L_B}, is therefore

$$\sigma(f|i) = \frac{\pi}{k^2(2L_A+1)(2L_B+1)} \sum_{J, M_J} \frac{N(f|E, J, M_J)N(i|E, J, M_J)}{\sum_f N(f|E, J, M_J)} \tag{124}$$

This is Light's statistical theory of reaction cross sections. The reader should consult the original papers $^{(41-44)}$ for detailed presentation and discussion of reaction cross sections calculated from Eq. (124). We shall make two remarks.

First, the reaction cross section is still indifferent to the nature of final vibrational energy: Two product levels differing only in the distribution of energy among vibrational modes will be reached with the same cross section. Rotation is another matter. Shifting energy from vibration to rotation affects the angular momentum coupling, in a complicated manner.

Second, when the rotational angular momentum of reactant and product molecules is small compared to the values of J that are important in Eq. (124)—that is, when the angular momentum in both entrance and exit channels is mainly orbital angular momentum of relative motion—the final state distribution can be calculated rather simply provided the sum in the denominator of Eq. (124) can be regarded as independent of (J, M_J). This sum is proportional to the total rate of decay of a complex with angular momentum quantum numbers (J, M_J) [the density of states of the complex entering the rate expression (92) will be independent of (J, M_J) for values of J that are important in Eq. (124) if the complex region is in fact a deep potential hole in the energy surface]. We assume, therefore, that the lifetime of the complex is independent of (J, M_J), and then the final state distribution is governed by

$$\sum_{J, M_J} \frac{N(f|E, J, M_J)N(i|E, J, M_J)}{(2L_A+1)(2L_B+1)} \tag{125}$$

Because J is essentially the orbital angular momentum in the entrance and exit channels, the sum over J is restricted to $\hbar J < l^*(E - E_i)$ and $\hbar J < l^*(E - E_f)$;

the upper limit in the sum is therefore the lesser of these two values. Call it J^*. For $J < J^*$ we can calculate the numbers $N(f|E, J, M_J)$ and $N(i|E, J, M_J)$, defined by Eq. (119), without restriction on the initial and final orbital angular momenta, for these are essentially J. One finds easily that

$$\sum_L N(f, L|J, M_J) = (2L_C + 1)(2L_D + 1)$$

$$\sum_L N(i, L|J, M_J) = (2L_A + 1)(2L_B + 1)$$

(126)

and therefore Eq. (125) becomes

$$\sum_{J, M_J} (2L_C + 1)(2L_D + 1) \simeq J^{*2}(2L_C + 1)(2L_D + 1) \tag{127}$$

The product $(2L_C + 1)(2L_D + 1)$ is of course just the degeneracy of the final vibration–rotation level. If the upper limit J^* is set by the orbital angular momentum restriction in the exit channel, then we have just the final state distribution given by the full microcanonical rate calculation [Eq. (110)]: Angular momentum of the complex places no restriction on the range of states available in the exit channel. If the upper limit J^* is set by the orbital angular momentum restriction in the entrance channel, however, the cross section to a given final state is independent of the energy of that state.

In particular we can calculate the distribution of low-lying product vibration–rotation states using Eq. (127), for these states, of course, have little rotational angular momentum. If J^* is set by the exit channel, we have the Maxwell–Boltzmann distribution derived above [Eq. (111)]; if J^* is set by the entrance channel we have a uniform distribution—that is, a Maxwell–Boltzmann distribution with infinite temperature.

ACKNOWLEDGMENTS

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Note Added in Proof

Two papers discussing nuclear symmetry restrictions on transition states (Section 2.4) have recently appeared: R. E. Stanton and J. W. McIver, Jr., Group theoretical selection rules for the transition states of chemical reactions, *J. Am. Chem. Soc.* **97**, 3632–3646 (1975); and P. Pechukas, On simple saddle points of a potential surface, the conservation of nuclear symmetry along paths of steepest descent, and the symmetry of transition states, *J. Chem. Phys.* **64**, 1516–1521 (1976).