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Publication Date
1976

Submitted to Journal of Chemical Physics

LBL-4912
Preprint c.1

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January 1976

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48

LBL-4912

UNIFIED STATISTICAL MODEL FOR 'COMPLEX' AND 'DIRECT' REACTION MECHANISMS*

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Abstract

A unified statistical theory for bimolecular chemical reactions is developed. In the limit of a "direct" mechanism it becomes the usual transition state theory, which is correct for this situation, and if the reaction proceeds via a long-lived collision complex it reduces to the statistical model of Light and Nikitin. A general criterion for locating the "dividing surfaces" that are central to statistical theory is also discussed. This prescription (Keck's variational principle) is shown not only to locate the usual dividing surfaces that pass through saddle points and minima of the potential energy surface, but it also selects the critical surfaces relevant to the "orbitting" and "non-adiabatic trapping" models of complex formation.

I. INTRODUCTION.

Recent work[1-5] on the transition state theory[6] of chemical reactions has exploited the fact that the fundamental dynamical assumption of transition state theory is that the reaction mechanism is "direct". Within the framework of classical mechanics this means that transition state theory is actually exact if there exists a surface, that divides reactant and product configuration space, through which no classical trajectory passes more than once.[7] Furthermore, for a simple reaction with a single saddle point separating reactants and products--such as the prototype $H + H_2 \rightarrow H_2 + H$ reaction--this assumption of direct dynamics is indeed true for energies not too far above threshold.[1,8] Progress has also been made in constructing a fully quantum mechanical version of this model which, unlike the conventional quantum mechanical version of transition state theory, does not require the Hamiltonian to be separable about the saddle point.[3-5]

All reactions are not "direct", however; many of them proceed by "complex" mechanisms, i.e., they form long-lived collision complexes.[9] Within the framework of classical mechanics this corresponds to classical trajectories that undergo a number of oscillations back and forth through the interaction region, and it is intuitively clear that in this situation there is no "dividing surface" through which all trajectories pass only once. The fundamental dynamical assumption of transition state theory is thus not valid.

There do exist statistical theories which are designed especially for describing "complex" reactions, the best known of these being associated with the work of Light[10] and Nikitin.[11] Because this approach explicitly incorporates the assumption of a long-lived collision complex, however, it becomes inapplicable when the reaction dynamics is "direct".

There are thus two kinds of statistical models for bimolecular reactions, transition state theory[6] which is appropriate for "direct" reaction dynamics, and the phase space theory[10,11] for "complex" reactions. The purpose of this paper is to construct a unified statistical theory which includes both of these models in the appropriate limiting cases.

This unified statistical theory is developed in Section II, and Section III discusses a general criterion for defining the "dividing surfaces" which separate reactants from products, or reactants and products from collision complexes. In addition to the simple case of a dividing surface through a saddle point or a minimum in the potential energy surface, the general criterion discussed in Section III is also shown to yield the dividing surfaces that are relevant to "orbitting" and "non-adiabatic" collision complexes, situations for which there are no actual saddle points on the (static) potential surface.

II. UNIFIED STATISTICAL THEORY.

For simplicity of presentation the initial development below (Sections IIa-IId) does not take explicit account of total angular momentum conservation; Section IIe gives the modifications of the final expressions that are necessary to take this into account. Also for simplicity, the figures are all drawn for the case of a collinear A + BC → AB + C reaction for which there are only two degrees of freedom. Sections IIa and IIb first summarize the usual transition state theory[6] for "direct" reactions and the phase space theory[10,11] for "complex" reactions, respectively, and Section IIc then constructs their synthesis. Classical mechanics is assumed throughout the paper although in most instances it is clear what the corresponding quantum mechanical expressions are.

a. "Direct" Mechanism

Figure 1 shows the sketch of a potential surface with a single saddle point separating reactants and products, the type for which the reaction mechanism will be "direct" at low energy. Transition state theory gives the rate constant for this reaction as[12]

$$k_{b\leftarrow a}(T) = (2\pi\hbar Q_a)^{-1} \int_0^\infty dE\ e^{-E/kT}\ N_o(E) \quad , \tag{2.1}$$

where "a" and "b" denote reactants and products, respectively, Q_a is the partition function per unit volume for non-interacting reactants, E is the total energy, and $N_o(E)$ is (proportional to) the microcanonical average of flux through the "dividing surface" S_o shown in Figure 1:

$$N_o(E) = 2\pi\hbar\ h^{-F} \int d\underset{\sim}{p} \int d\underset{\sim}{q}\ \delta[E-H(\underset{\sim}{p},\underset{\sim}{q})]\ \delta[f_o(q)]\ \frac{\partial f_o}{\partial \underset{\sim}{q}}\cdot\underset{\sim}{p}/\mu\ h(\frac{\partial f_o}{\partial \underset{\sim}{q}}\cdot\underset{\sim}{p}) \ . \quad (2.2)$$

In Eq. (2.2) $H(\underset{\sim}{p},\underset{\sim}{q})$ is the total (classical) Hamiltonian function, $f_o(\underset{\sim}{q})$ is the function of coordinates which defines the dividing surface S_o via the equation

$$S_o\text{:}\quad f_o(\underset{\sim}{q}) = 0 \quad , \qquad (2.3)$$

and h( ) is the unit step function,

$$h(x) = 1,\ x > 0$$
$$\qquad 0,\ x < 0 \quad ;$$

F is the number of degrees of freedom, and $(\underset{\sim}{p},\underset{\sim}{q}) = (p_i,q_i)$, $i = 1, \ldots, F$ are the cartesian coordinates of the system; for the collinear system illustrated in Figure 1 F = 2. The factor $\frac{\partial f_o}{\partial \underset{\sim}{q}}\cdot\underset{\sim}{p}/\mu$ in Eq. (2.2) is the expression for $\frac{df_o}{dt}$ in terms of the cartesian coordinates and momentum $(\underset{\sim}{p},\underset{\sim}{q})$; if it should be more convenient to choose non-cartesian coordinates and momenta in order to evaluate the phase space integral, then this factor is given more generally by

$$\frac{d}{dt} f_o(\underset{\sim}{q}) = \frac{\partial f_o}{\partial \underset{\sim}{q}} \cdot \frac{\partial H(\underset{\sim}{p},\underset{\sim}{q})}{\partial \underset{\sim}{p}} \quad .$$

For interpretational reasons it is useful to multiply and divide the integrand of Eq. (2.1) by $N_a(E)$, so that it reads

$$k_{b\leftarrow a} = (2\pi\hbar Q_a)^{-1} \int_0^\infty dE\ e^{-E/kT}\ P_{b\leftarrow a}(E)\ N_a(E) \qquad (2.4)$$

with

$$P_{b\leftarrow a}(E) \equiv N_o(E)/N_a(E) \quad , \tag{2.5}$$

where $N_a(E)$ is the microcanonical flux through the surface S_a (cf. Fig. 1) which lies far out in the reactant region. $N_a(E)$ is given by an expression identical to Eq. (2.2) with $f_o(\underset{\sim}{q})$ replaced by $f_a(\underset{\sim}{q})$, the function which defines surface S_a via the equation

$$S_a\text{:}\quad f_a(\underset{\sim}{q}) = 0 \quad . \tag{2.6}$$

$P_{b\leftarrow a}(E)$, defined by Eq. (2.5) as the ratio of reactive flux to incident flux, has the interpretation of an average <u>reaction probability</u>.[13,14]

It is useful to note that the flux integrals N_o and N_a introduced above have an alternate, more common interpretation than that of microcanonical flux through surfaces S_o and S_a. Thus consider the generic expression for N_o or N_a,

$$N(E) = 2\pi\hbar\; h^{-F} \int d\underset{\sim}{p} \int d\underset{\sim}{q} \quad \delta[E-H(\underset{\sim}{p},\underset{\sim}{q})]\; \delta[f(\underset{\sim}{q})]\; \frac{\partial f}{\partial \underset{\sim}{q}}\cdot\underset{\sim}{p}/\mu \; h(\frac{\partial f}{\partial \underset{\sim}{q}}\cdot\underset{\sim}{p}) \; . \tag{2.7}$$

Let the coordinates $\underset{\sim}{q} = \{q_i\}$, $i = 1, \ldots, F$ be chosen so that q_F measures distance away from the surface, and $\{q_i\}$, $i = 1, \ldots, F-1$ measure displacements on the F-1 dimensional surface. The function $f(\underset{\sim}{q})$ is then given by

$$f(\underset{\sim}{q}) = q_F \quad , \tag{2.8}$$

and in properly scaled coordinates the Hamiltonian is

$$H(\underset{\sim}{p},\underset{\sim}{q}) = \frac{{p_F}^2}{2\mu} + \sum_{i=1}^{F-1} \frac{{p_i}^2}{2\mu} + V(q_1, \ldots, q_{F-1}, q_F) \quad , \tag{2.9}$$

so that Eq. (2.7) becomes

$$N(E) = h^{-(F-1)} \int d\underset{\sim}{p}' \int d\underset{\sim}{q}' \int dp_F \int dq_F \quad \delta[E - H_{F-1}(\underset{\sim}{p}',\underset{\sim}{q}') - \frac{p_F^{\,2}}{2\mu}]$$
$$\times\ \delta(q_F)\ (\frac{p_F}{\mu})\ h(p_F) \quad , \qquad (2.10)$$

where $(\underset{\sim}{p}',\underset{\sim}{q}') = (p_i,q_i)$, $i = 1, \ldots, F-1$ and H_{F-1} is the Hamiltonian with the $F^{\underline{th}}$ degree of freedom removed, i.e., the Hamiltonian <u>on</u> the surface:

$$H_{F-1}(\underset{\sim}{p}',\underset{\sim}{q}') = \sum_{i=1}^{F-1} p_i^{\,2}/2\mu + V(q_1, \ldots, q_{F-1}, 0) \quad . \qquad (2.11)$$

The integrals over q_F and p_F are trivial, and one obtains

$$N(E) = h^{-(F-1)} \int d\underset{\sim}{p}' \int d\underset{\sim}{q}' \quad h[E - H_{F-1}(\underset{\sim}{p}',\underset{\sim}{q}')] \quad , \qquad (2.12)$$

which is recognized as the microcanonical partition function--i.e., the number of quantum states with energy less than or equal to E--for the reduced system of F-1 degrees of freedom. This identification of the flux integral N(E) as the number of quantum states (in the statistical mechanical sense) on the dividing surface--which is only rigorously valid within classical mechanics--is also the way in which these statistical theories are usually "quantized": Eq. (2.12) is replaced by counting discrete energy levels to determine the number of quantum states with energy below E.

B. <u>"Complex" Mechanism</u>

Figure 2 shows the sketch of a potential energy surface that has an attractive well in the A-B-C region of configuration space, corresponding to a stable triatomic molecule. In Fig. 2 this region of the collision complex is separated from reactants and products by two saddle points, but the following analysis also applies if there are no such saddle points, i.e., if the potential surface is monotonically "downhill" from reactants and products toward the well.

The "phase space theory"[10,11] for describing collision complexes has the form of competing first order rate processes. The rate constant is given by an expression similar to Eq. (2.1) with the flux integral N_o replaced according to

$$N_o(E) \longrightarrow \frac{N_1(E)\ N_2(E)}{N_1(E)+N_2(E)} \quad , \tag{2.13}$$

where N_1 and N_2 are the flux integrals through surfaces S_1 and S_2 (cf. Fig. 2), respectively;

$$k_{b\leftarrow a} = (2\pi\hbar\ Q_a)^{-1} \int_0^\infty dE\ e^{-E/kT}\ \frac{N_1(E)\ N_2(E)}{N_1(E)+N_2(E)} \quad . \tag{2.14}$$

(If there are no saddle point regions separating the well in the potential surface from the asymptotic regions, then the surfaces S_1 and S_2 are shifted to their asymptotic regions, i.e., $S_1 \to S_a$, $S_2 \to S_b$, so that in Eq. (2.14) $N_1 \to N_a$, $N_2 \to N_b$.) It is customary in the statistical model of long-lived collision complexes to think of N_1 and N_2 as the number of internal states on surfaces S_1 and S_2, but as noted in the last paragraph of Section IIa, this is equivalent to their interpretation as fluxes.

Again, for interpretational reasons, one multiplies and divides the integrand in Eq. (2.14) by common factors so that the rate constant in Eq. (2.4) is given by Eq. (2.4), but where the net reaction probability is now given by

$$P_{b\leftarrow a}(E) = \frac{P_{b\leftarrow x}\ P_{x\leftarrow a}}{P_{b\leftarrow x}+P_{a\leftarrow x}} \quad , \tag{2.15}$$

where

$$P_{x\leftarrow a}(E) = N_1(E)/N_a(E) \qquad (2.16a)$$

$$P_{a\leftarrow x}(E) = N_1(E)/N_x(E) \qquad (2.16b)$$

$$P_{b\leftarrow x}(E) = N_2(E)/N_x(E) \quad , \qquad (2.16c)$$

N_1, N_2, and N_x being the flux integrals through surfaces S_1, S_2, and S_x, respectively, in Fig. 2. $P_{x\leftarrow a}$, $P_{a\leftarrow x}$, and $P_{b\leftarrow x}$ have the interpretations of the probability of reactants "a" forming a collision complex "x", the probability that the complex decays back to reactants, and the probability that the complex decays to products "b", respectively. (Note that the flux integral N_x actually cancels out in the equation for $P_{b\leftarrow a}$.) The net reaction probability $P_{b\leftarrow a}$ thus has the usual form[15] of the probability that reactants from a collision complex, $P_{x\leftarrow a}$, times the branching ratio $P_{b\leftarrow x}/(P_{b\leftarrow x}+P_{b\leftarrow x})$ for the complex breaking up to give products.

c. Unified Theory

To summarize the results of Sections IIa and IIb, the rate constant is in general given by

$$k_{b\leftarrow a} = (2\pi\hbar\ Q_a)^{-1} \int_0^\infty dE\ e^{-E/kT}\ P_{b\leftarrow a}(E)\ N_a(E) \quad , \qquad (2.4)$$

where in the "direct" case one has

$$P_{b\leftarrow a}^{\text{direct}} = (N_o/N_a) \quad , \qquad (2.5)$$

and in the "complex" case

$$P_{b\leftarrow a}^{\text{complex}} = \frac{P_{b\leftarrow x}\ P_{x\leftarrow a}}{P_{b\leftarrow x}+P_{a\leftarrow x}} \tag{2.15}$$

$$= \frac{(N_2/N_x)\ (N_1/N_a)}{(N_2/N_x)+(N_1/N_x)} \quad , \tag{2.15$'$}$$

where the various flux integrals N(E) are all of the form of Eq. (2.7) for the various surfaces indicated in Figures 1 and 2.

$P_{b\leftarrow a}^{\text{direct}}$ in Eq. (2.5) is clearly inapplicable to the "complex" situation, and $P_{b\leftarrow a}^{\text{complex}}$ in Eq. (2.15) is also incorrect in the "direct" limit. To see this, suppose the potential surface in Fig. 2 is distorted so that the well is raised and the saddle point through which S_2 passes is diminished, so much so that the well and saddle point merge and disappear. In this limit the potential surface reverts to one with a single saddle point, i.e., the "direct" type in Fig. 1; surfaces S_2 and S_x in Fig. 2 merge so that $N_2 \equiv N_x$, and N_1, the flux through the remaining saddle point, is what is designated N_o in Fig. 1. The reaction probability given by the "complex" prescription in Eq. (2.15$'$) thus becomes

$$P_{b\leftarrow a}^{\text{complex}} \rightarrow \frac{(1)(N_o/N_a)}{1 + (N_o/N_a)} \quad , \tag{2.17}$$

which is not the correct result, Eq. (2.5), for the "direct" case.

The reason that Eq. (2.15$'$) fails in the "direct" limit is clear--the existence of a long-lived collision complex necessarily implies that

$$P_{b\leftarrow x},\ P_{a\leftarrow x} << 1 \quad , \tag{2.18}$$

otherwise the collision complex would not be long-lived. In the "direct" limit considered above, however, $P_{b\leftarrow x} \rightarrow 1$, which is physically correct but which violates Eq. (2.18), an assumption implicit in Eq. (2.15).

To construct a theory capable of describing both "direct" and "complex" limits, therefore, it is necessary to define a net reaction probability $P_{b\leftarrow a}$ that is valid for all values of $P_{x\leftarrow a}$, $P_{a\leftarrow x}$, and $P_{b\leftarrow x}$ between 0 and 1. This is accomplished by using the probability branching analysis of Hirschfelder and Wigner.[16] A sketch of the branching picture is given in Fig. 3, and the net reaction probability is the sum of the reaction probabilities for all the possible branches:

$$P_{b\leftarrow a} = \sum_{n=0}^{\infty} P_{b\leftarrow x} \, (1-P_{b\leftarrow x})^n \, (1-P_{a\leftarrow x})^n \, P_{x\leftarrow a} \quad . \tag{2.19}$$

The $n^{\underline{th}}$ term in Eq. (2.19) corresponds to a collision complex that has survived n oscillations back and forth between surfaces S_1 and S_2; the probability of this branch is the product of the probability of forming the collision complex from reactants, $P_{x\leftarrow a}$, the probability that the complex does not decay to reactants or products on n encounters at surfaces S_1 and S_2, $(1-P_{b\leftarrow x})^n \, (1-P_{a\leftarrow x})^n$, and the probability that the complex decays to products, $P_{b\leftarrow x}$. This geometric series is easily summed to give[16]

$$P_{b\leftarrow a} = \frac{P_{b\leftarrow x} \, P_{x\leftarrow a}}{1-(1-P_{b\leftarrow x})(1-P_{a\leftarrow x})}$$

$$= \frac{P_{b\leftarrow x} \, P_{x\leftarrow a}}{P_{b\leftarrow x}+P_{a\leftarrow x} - P_{b\leftarrow x}P_{a\leftarrow x}} \tag{2.20a}$$

$$= \frac{(N_2/N_x)(N_1/N_a)}{(N_2/N_x)+(N_1/N_x) - (N_2/N_x)(N_1/N_x)} \quad . \tag{2.20b}$$

The Appendix shows that Eq. (2.20) also results from a WKB treatment of transmission through a double barrier potential.

Eq. (2.20) is seen to differ from Eq. (2.15) only by the term in the denominator which is quadratic in probability. For a long-lived collision complex, for which Eq. (2.18) holds, this quadratic term will be neglible compared to the two linear terms, so that Eq. (2.15) is recovered in the "complex" limit. On the other hand, in the "direct" limit described above--for which $N_2 \rightarrow N_x$ so that $P_{b\leftarrow x} \rightarrow 1$, and $N_1 \equiv N_o$--Eq. (2.20) gives

$$P_{b\leftarrow a} = \frac{(1)\ (N_o/N_a)}{1 + P_{a\leftarrow x} - (1)\ P_{a\leftarrow x}}$$

$$= (N_o/N_a) \quad ,$$

which is Eq. (2.5), the correct result for the case of a "direct" reaction.

Eq. (2.20), therefore, is the desired result; it reduces to the correct "direct" and "complex" expressions in the appropriate limits. Inserting Eq. (2.20) into Eq. (2.4) gives the following expression for the rate constant in this unified statistical theory:

$$k_{b\leftarrow a} = (2\pi\hbar\ Q_a)^{-1} \int_0^\infty dE\ e^{-E/kT} \frac{N_2(E)N_1(E)}{N_2(E)+N_1(E) - N_2(E)N_1(E)/N_x(E)} \ , \qquad (2.21)$$

and one sees that, unlike Eq. (2.14), the flux integral $N_x(E)$--the flux "out of" the collision complex--does not cancel out in this more general expression.

d. Collinear Harmonic Case

In many actual applications of these statistical expressions the flux integrals N(E) are evaluated by approximating the potential surface as quadratic about the saddle points (and minima). Thus it is interesting and illustrative to see the explicit form taken by the reaction probability in the simplest case, a collinear A + BC → AB + C reaction within the harmonic approximation.

In this case the generic flux integral N(E) is

$$N(E) = (E-V)/\hbar\omega \quad , \qquad (2.22)$$

where V is the potential energy of the saddle point (or minimum), and ω is the harmonic frequency for the direction along the relevant surface S, i.e., for the vibrational motion perpendicular to the reaction coordinate.

For the case of a single barrier, as in Fig. 1, transition state theory, Eq. (2.5), thus gives

$$P^{\text{direct}}_{b\leftarrow a}(E) = \frac{\omega_a}{\omega_o} \cdot \frac{E-V_o}{E} \quad , \qquad (2.23)$$

where ω_a and ω_o are the vibrational frequencies of the reactant molecule BC and the symmetric stretch of the "activated complex", respectively, V_o is the potential energy of the saddle point, and where the zero of total energy is chosen as the bottom of the reactant valley. Eq. (2.23) is a well-known result.[13,14]

For the potential surface sketched in Fig. 2, which has a stable collision complex separated from reactants and products by saddle points, the phase space model for a long-lived collision complex, Eq. (2.15') gives

$$P_{b\leftarrow a}^{\text{complex}} = \frac{\omega_a}{\omega_1+\omega_2} \frac{(E-V_1)(E-V_2)}{E(E-\bar{V})} \qquad (2.24a)$$

with

$$\bar{V} \equiv \frac{\omega_2 V_1+\omega_1 V_2}{\omega_2+\omega_1} \quad , \qquad (2.24b)$$

where V_1 and ω_1, and V_2 and ω_2, are the potential and frequency for saddle points 1 and 2, respectively. If the potential surface is symmetric--i.e., $V_2 = V_1$, $\omega_2 = \omega_1$--then Eq. (2.24) simplifies the

$$P_{b\leftarrow a}^{\text{complex}} = \frac{1}{2} \frac{\omega_a}{\omega_1} \frac{E-V_1}{E} \quad , \qquad (2.25)$$

which is similar to Eq. (2.23) but with the additional factor of $\frac{1}{2}$; this is the "transmission coefficient" implicit in the phase space theory[10,11] since it assumes that the complex breaks up equally likely to give products or reactants.

The unified statistical theory, Eq. (2.20), on the other hand, gives the reaction probability in the symmetrical case as

$$P_{b\leftarrow a}^{\text{unified}} = \left(2 - \frac{\omega_x}{\omega_1} \frac{E-V_1}{E-V_x}\right)^{-1} \frac{\omega_a}{\omega_1} \frac{E-V_1}{E} \quad , \qquad (2.26)$$

where V_x and ω_x are the potential energy and frequency for the minimum of the potential (cf. Fig. 2). This expression may be thought of as Eq. (2.25) with the addition of an energy-dependent "transmission coefficient"

$$\left(2 - \frac{\omega_x}{\omega_1}\,\frac{E-V_1}{E-V_x}\right)^{-1} \quad . \tag{2.27}$$

For low energies and strongly bound complexes one has

$$\frac{E-V_1}{E-V_x} << 1 \quad ,$$

so that

$$2 - \frac{\omega_x}{\omega_1}\,\frac{E-V_1}{E-V_x} \simeq 2 \quad ,$$

and Eq. (2.26) thus reduces to Eq. (2.25) in this limit. In the "direct" limit that the well in the potential surface becomes shallow and disappears--i.e., $V_x \to V_1$, $\omega_x \to \omega_1$--one has

$$2 - \frac{\omega_x}{\omega_1}\,\frac{E-V_1}{E-V_x} \to 2 - 1 = 1 \quad ,$$

so that Eq. (2.26) also reduces to the correct result, Eq. (2.23), in this limit.

e. Reactions in Three Dimensions; Conservation of Total Angular Momentum

To take explicit account of total angular momentum conservation, which is necessary when treating reactions in three dimensional space, Eq. (2.4) is replaced by

$$k_{b\leftarrow a} = (2\pi\hbar\ Q_a)^{-1} \int_0^\infty dE\ \ e^{-E/kT} \int_0^\infty dJ\ 2J\ P_{b\leftarrow a}(E,J)\ N_a(E,J) \quad , \tag{2.28}$$

where $P_{b\leftarrow a}(E,J)$ is the net reaction probability for total energy E and total angular momentum J. $P_{b\leftarrow a}(E,J)$ is given in terms of flux integrals by precisely the same expressions as in Sections IIa-IIc but where the flux integrals are now for a specific value of total angular momentum as well as total energy and have the generic form

$$N(E,J) = 2\pi\hbar\ h^{-F} \int d\underset{\sim}{p} \int d\underset{\sim}{q}\quad \delta[E-H(\underset{\sim}{p},\underset{\sim}{q})]\ \delta[J-\mathcal{J}(\underset{\sim}{p},\underset{\sim}{q})]$$

$$\times\ \delta[M-\mathcal{M}(\underset{\sim}{p},\underset{\sim}{q})]\ \delta[f(\underset{\sim}{q})]\ \frac{\partial f}{\partial \underset{\sim}{q}}\cdot\underset{\sim}{p}/\mu\ h(\frac{\partial f}{\partial \underset{\sim}{q}}\cdot\underset{\sim}{p}) \quad . \qquad (2.29)$$

$\mathcal{J}(\underset{\sim}{p},\underset{\sim}{q})$ and $\mathcal{M}(\underset{\sim}{p},\underset{\sim}{q})$ in Eq. (2.29) are the total angular momentum and its component along a space-fixed axis, respectively, expressed in terms of the phase space integration variables $(\underset{\sim}{p},\underset{\sim}{q})$; M may have any value between -J and J since the flux integrals are independent of it.

III. SPECIFICATION OF DIVIDING SURFACES.

A central role is played in the expressions of the previous section by the "dividing surfaces" through which the various flux integrals are calculated. This section explores in more detail the precise way in which these surfaces can be defined. It is important that the general definition applies not only to the simple case that the potential energy surface has actual saddle points and minima, but also includes the dividing surfaces which define collision complexes within the "orbitting" and "non-adiabatic trapping" models, which are unrelated to saddle points or minima of the (static) potential energy surface.

The most general and rigorous way of defining the dividing surfaces is by Keck's[17] variational principle, i.e., so that $N_o(E)$ in Fig. 1, and N_1 and N_2 in Fig. 2, are relative minima of flux in the reactive direction, i.e., so that they are the "bottlenecks" of the reaction. It is then also natural to define S_x in Fig. 2 so that N_x is a relative maximum of flux.

To see this more clearly, consider the continuous family of dividing surfaces S_ρ, sketched in Fig. 4, which are parameterized by the "reaction coordinate" ρ, the arc length along the reaction path (curve C in Fig. 4). S_ρ is the dividing surface perpendicular to curve C at the distance ρ along C.

Considering first the collinear A + BC → AB + C reaction, suppose the potential energy surface is harmonic in the degree of freedom perpendicular to the reaction path; in natural collision coordinates[18] the potential surface is given within this harmonic approximation by

$$V(\rho,u) = V_o(\rho) + \frac{1}{2}k(\rho)u^2 \quad , \tag{3.1}$$

where u is the vibrational coordinate, the degree of freedom perpendicular to the reaction path, and $k(\rho)$ is the force constant for this vibrational mode at position ρ along the reaction path. As discussed in Section IId, the flux integral through surface S_ρ, $N_\rho(E)$, is then given by

$$N_\rho(E) = \frac{E-V_o(\rho)}{\hbar\omega(\rho)} \quad , \tag{3.2}$$

where $\omega(\rho)$ is the vibrational frequency for the u-motion at position ρ

$$\omega(\rho) = \sqrt{\frac{k(\rho)}{\mu}} \quad . \tag{3.3}$$

If it is first assumed that $\omega(\rho)$ does not change significantly with ρ, then it is clear from Eq. (3.2) that N_ρ has a relative minimum (maximum) of those values of ρ for which $V_o(\rho)$ has a relative maximum (minimum). For the potential surfaces sketched in Figures 1 and 2 $N_\rho(E)$ has the form sketched in Figures 5a and 5b respectively. The flux integrals N_0 of Fig. 1, and N_1, N_2, and N_x of Fig. 2, are the values of N_ρ at ρ_o (in Fig. 5a) and ρ_1, ρ_2, ρ_x (in Fig. 5b). As suggested above, therefore, N_0, N_1, and N_2 are relative minima ("bottlenecks") of the flux along the reaction path, and N_x is a relative maximum.

Eq. (3.2) can also be used to illustrate the phenomenon of "non-adiabatic trapping"[19,20] which results if $\omega(\rho)$ varies strongly along the reaction path. Consider a potential surface of the type sketched in Fig. 1. Typically the vibrational mode "relaxes" in the region of the saddle point, i.e., $\omega(\rho)$

has a minimum at $\rho = 0$. (For the $H + H_2$ reaction[20] $\omega(0) \simeq \frac{1}{2}\,\omega(\infty)$.) Fig. 6 shows a sketch of the two factors that contribute to $N_\rho(E)$, $E-V_o(\rho)$ and $^1/\omega(\rho)$, and one can clearly see that if $1/\omega(\rho)$ is sufficiently sharply peaked, then $N_\rho(E)$ will have the same qualitative shape as in Fig. 5b--i.e., there can be two bottleneck regions (minima in N_ρ) on either side of the actual saddle point of the potential surface. This qualitative explanation of "non-adiabatic trapping" in terms of relaxation of the vibrational mode about the saddle point is usually[20,21] based on the assumption of vibrational adiabaticity. It is very interesting to see here that it also comes out of a purely statistical theory when the vibrational criterion is used to locate the relevant dividing surfaces.

Finally, to show that the variational criterion also predicts the correct dividing surface for the "orbitting model" of collision complexes it is necessary to consider a three dimensional system, $A + BC \rightarrow AB + C$ for example. As discussed in Section IIe, for reactions in three dimensions the flux integrals must be defined for a given value of total angular momentum J as well as total energy E. In the orbitting model the reaction coordinate is taken to be the radial coordinate R, the distance between A and the center of mass of BC, and the interaction potential between A + BC is assumed to be a function only of R (usually the van der Waals type $-C/R^6$). The A + BC system in its overall center of mass has six degrees of freedom, and the 12-dimensional integral in Eq. (2.29) is most conveniently evaluated if the six pair of coordinates and momenta are chosen as the following action-action variables:[22,23]

(P,R): radial motion of A - BC

(ℓ,q_ℓ): orbital angular momentum of A relative to BC

(j,q_j): rotational angular momentum of BC
(n,q_n): vibrational motion of BC
(J,q_J): total angular momentum
(M,q_M): projection of total angular momentum.

The flux integral [Eq. (2.29)] through the dividing surface located at the value R of the radial coordinate is then given by (setting $\hbar = 1$)

$$N_R(E,J) = (2\pi)^{-5} \int_0^\infty dn \int_0^\infty dj \int_0^\infty dJ' \int_{-J'}^{J'} dM' \int_{(J'-j)}^{J'+j} d\ell \int_{-\infty}^{\infty} dP \int_0^\infty dR'$$

$$\times \int_0^{2\pi} dq_n \int_0^{2\pi} dq_j \int_0^{2\pi} dq_J \int_0^{2\pi} dq_M \int_0^{2\pi} dq_\ell \;\; \delta(E-H)\;\delta(J-J')\;\delta(M-M')$$

$$\times \;\; \delta(R-R') \;\; \frac{P}{\mu}\, h(P) \quad , \qquad (3.4)$$

where the Hamiltonian in these variables is[23]

$$H = \frac{P^2}{2\mu} + \frac{\ell^2}{2\mu R^2} + V(R) + \varepsilon(n,j) \quad , \qquad (3.5)$$

$\varepsilon(n,j)$ being the vibration/rotation energy of BC in terms of the "quantum numbers" (actually action variables) n and j. Since the integrand of Eq. (3.4) is independent of the five angle variables, the integral over them is trivial, and the delta functions allow one to do the integrals over R, P, J', and M', yielding

$$N_R(E,J) = \int_0^\infty dn \int_0^\infty dj \int_{|J-j|}^{J+j} d\ell \quad h\left(E-V(R) - \varepsilon(n,j) - \frac{\ell^2}{2\mu R^2}\right); \qquad (3.6)$$

the limits on the ℓ-integral are the usual "triangle relation" involving the angular momenta ℓ, j, and J.

In most applications of the orbitting model it is also assumed that most of the angular momentum is orbital, i.e.,

$$\ell >> j \quad , \tag{3.7a}$$

so that

$$\ell \simeq J \quad , \tag{3.7b}$$

whereby Eq. (3.6) becomes

$$N_R(E,J) = \int_0^\infty dn \int_0^\infty dj \; 2j \; h[E-V(R) - \frac{J^2}{2\mu R^2} - \varepsilon(n,j)] \tag{3.8a}$$

$$\equiv W(E-V(R) - \frac{J^2}{2\mu R^2}) \quad , \tag{3.8b}$$

where the function $W(\bar{E})$ is defined by

$$W(\bar{E}) = \int_0^\infty dn \int_0^\infty dj \; 2j \; h[\bar{E}-\varepsilon(n,j)] \quad . \tag{3.9}$$

$W(\bar{E})$ is thus the number of quantum states of the diatomic molecule BC with energy below $\bar{E}$, i.e., the microcanonical partition function of BC. $W(\bar{E})$ is a strictly increasing function of $\bar{E}$--if BC is approximated as a rigid rotor-harmonic oscillator, for example, $W(\bar{E}) \propto \bar{E}^2$--so that the value of R which makes $N_R(E,j)$ an extremum is

$$0 = \frac{\partial}{\partial R} N_R(E,J) \tag{3.10}$$

$$= - W'(E-V(R) - \frac{J^2}{2\mu R^2}) \frac{\partial}{\partial R} (V(R) + \frac{J^2}{2\mu R^2}) \quad ,$$

or since $W' > 0$, the condition is

$$0 = \frac{\partial}{\partial R} (V(R) + \frac{J^2}{2\mu R^2}) \quad ; \qquad (3.11)$$

i.e., the dividing surface which makes the flux a minimum is at that value of R for which the "effective potential" $V(R) + J^2/2\mu R^2$ has a maximum, and this is the usual criterion of the orbitting model. It should be noted, though, that even when the approximations in Eq. (3.7) are not valid, Eq. (3.6) is still the correct expression for $N_R(E,J)$ (although the integrals are somewhat messier to evaluate[15]) and the optimum choice for R can still be determined variationally, i.e., by Eq. (3.10).

One thus sees that the variational criterion for choosing the dividing surface provides a unified prescription that correctly describes these several quite different physical situations.

IV. SUMMARY AND CONCLUDING REMARKS.

Section II has presented a unified statistical theory of bimolecular reactions that includes as special limiting cases the usual transition state theory, which is appropriate for a "direct" reaction mechanism, and the phase space theory of Light and Nikitin, which is appropriate for reactions that proceed via a long-lived collision complex. The theory is completely non-empirical, i.e., it involves the potential energy surface of the reacting system but has no empirical parameters. Since this unified theory is correct in the limit of a completely "direct" mechanism and that of a long-lived collision complex, one can perhaps reasonably hope that it will also be useful for intermediate situations.

The variational criterion[17] for choosing the relevant "dividing surfaces" which appear in the theory is discussed in Section III. In addition to yielding the usual dividing surfaces that are related to saddle points and minima in the potential energy surface, this general criterion is seen also to produce the critical surfaces relevant to the "orbitting model" and also that which describes "non-adiabatic trapping". It thus appears that this unified statistical theory, together with the variational criterion for locating the dividing surfaces, is capable of describing a wide variety of different kinds of dynamical phenomena in chemical reactions.

ACKNOWLEDGMENT

I would like to thank Dr. Carl Moser of the Centre Européen de Calcul Atomique et Moléculaire, Orsay, for his warm hospitality at the workshop on "Collisions on Potential Energy Surfaces of Excited States", July 7 - September 5, 1975, during which time this work began.

APPENDIX: DERIVATION OF EQ. (2.20) VIA THE WKB APPROXIMATION

It is interesting to see that the fundamental equation of the unified statistical model, Eq. (2.20), is also obtained by a WKB treatment of transmission by a double barrier potential.

Consider the one-dimensional potential sketched in Fig. 6, where E is the collision energy. θ_1 and θ_2 are the barrier penetration integrals through barriers 1 and 2, and ϕ is the phase integral across the potential well:

$$\theta_1 = \int_{x_1}^{x_2} dx \sqrt{2\mu[V(x)-E]/\hbar^2}$$

$$\theta_2 = \int_{x_3}^{x_4} dx \sqrt{2\mu[V(x)-E]/\hbar^2}$$

$$\phi = \int_{x_2}^{x_3} dx \sqrt{2\mu[E-V(x)]/\hbar^2} \quad .$$

The WKB approximation for the transmission probability has been considered by Child,[24] and the general result can be written in the following simple form

$$P(E) = \frac{p_1 p_2}{1+(1-p_1)(1-p_2) + 2\sqrt{1-p_1}\sqrt{1-p_2} \cos 2\phi} \quad , \qquad \text{(A.1)}$$

where p_1 and p_2 are the WKB tunneling probabilities through barriers 1 and 2:

$$p_i = \frac{1}{1+e^{2\theta_i}} \quad , \; i = 1,2 \quad . \tag{A.2}$$

As a function of energy E, P(E) in Eq. (A.1) has a resonance structure that is uninteresting for purposes of determining an average transmission probability. This average transmission probability $\bar{P}(E)$--which corresponds to averaging P(E) over an energy interval that contains many individual resonances but which is still small compared to the energy variation of $\bar{P}(E)$--can be obtained by averaging Eq. (A.1) over ϕ:

$$\bar{P}(E) = \frac{1}{\pi} \int_0^{\pi} d\phi \; \frac{p_1 p_2}{1+(1-p_1)(1-p_2) + 2\sqrt{1-p_1}\sqrt{1-p_2}\,\cos 2\phi} \quad , \tag{A.3}$$

and it is easy to show that this gives

$$\bar{P}(E) = \frac{p_1 p_2}{1-(1-p_1)(1-p_2)} = \frac{p_1 p_2}{p_1+p_2 - p_1 p_2} \quad , \tag{A.4}$$

which is the form of Eq. (2.20). If $p_1, p_2 << 1$, then Eq. (A.4) becomes

$$\bar{P}(E) \simeq \frac{p_1 p_2}{p_1+p_2} \quad ,$$

corresponding to a long-lived collision complex, and if $p_i \to 1$, then it becomes

$$\bar{P}(E) \simeq p_j \quad (j \neq i) \quad ,$$

the "direct" limit.

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* Supported in part by the U.S. Energy Research and Development Administration, and by the National Science Foundation under grant GP-41509X.

† Camille and Henry Dreyfus Teacher-Scholar; J. S. Guggenheim Memorial Fellow on sabbatical leave from the Department of Chemistry, University of California, Berkeley, CA 94720.

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FIGURE CAPTIONS

Figure 1. Sketch of a potential energy surface for a collinear A + BC → AB + C reaction that has a single saddle point separating reactants and products. Curve C is the "reaction path", and S_o and S_a are "dividing surfaces" perpendicular to it, S_o through the saddle point and S_a far out in the reactant region.

Figure 2. Sketch of a potential energy surface for a collinear A + BC → AB + C reaction that has an attractive well, corresponding to a stable ABC molecule, that is separated from reactants and products by saddle points. Curve C is the reaction path, and the dividing surfaces S_1 and S_2 cross it through the saddle points, S_x through the minimum of the potential well, and S_a and S_b in the reactant and product regions, respectively.

Figure 3. Sketch of the flow of probability from reactants "a" through the complex "x" to products "b". $P_{x\leftarrow a}$, $P_{a\leftarrow x}$, and $P_{b\leftarrow x}$ are the transition probabilities between the indicated regions for a given encounter at one of the "dividing surfaces", S_1 and S_2.

Figure 4. Sketch of a potential energy surface indicating the reaction path C and reaction coordinate ρ, the arc length along C. S_ρ is a "dividing surface" that crosses C at the value ρ of the reaction coordinate.

Figure 5. The flux integral $N_\rho(E)$ through surface S_ρ, as a function of ρ, for a potential surface of the type in (a) Fig. 1 and (b) Fig. 2.

Figure 6. Sketch of the two factors that contribute to Eq. (3.2), for a potential surface of the type in Fig. 1.

Figure 7. A one-dimensional double barrier potential function; E is the collision energy.

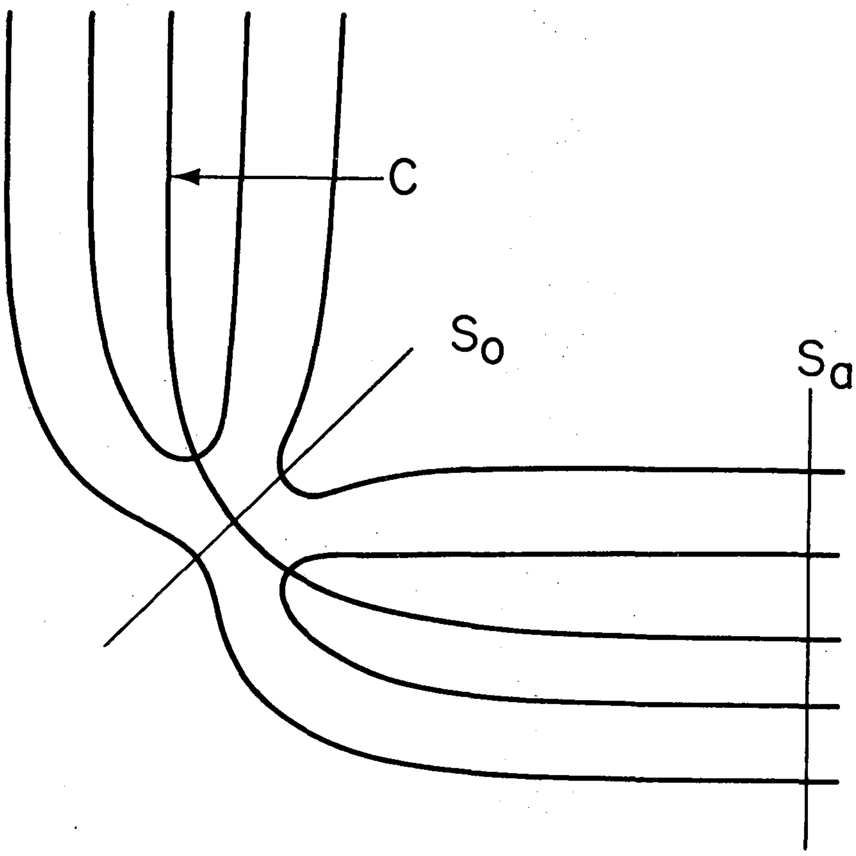

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Figure 1

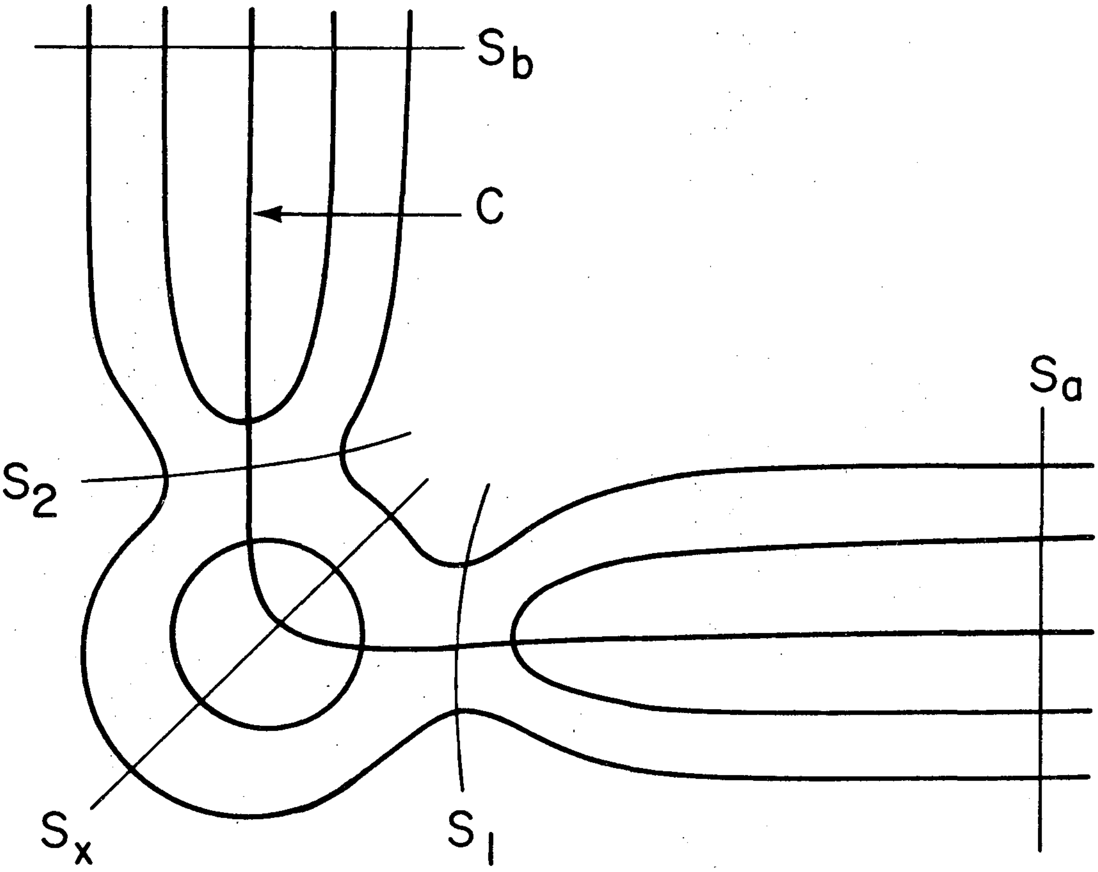

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Figure 2

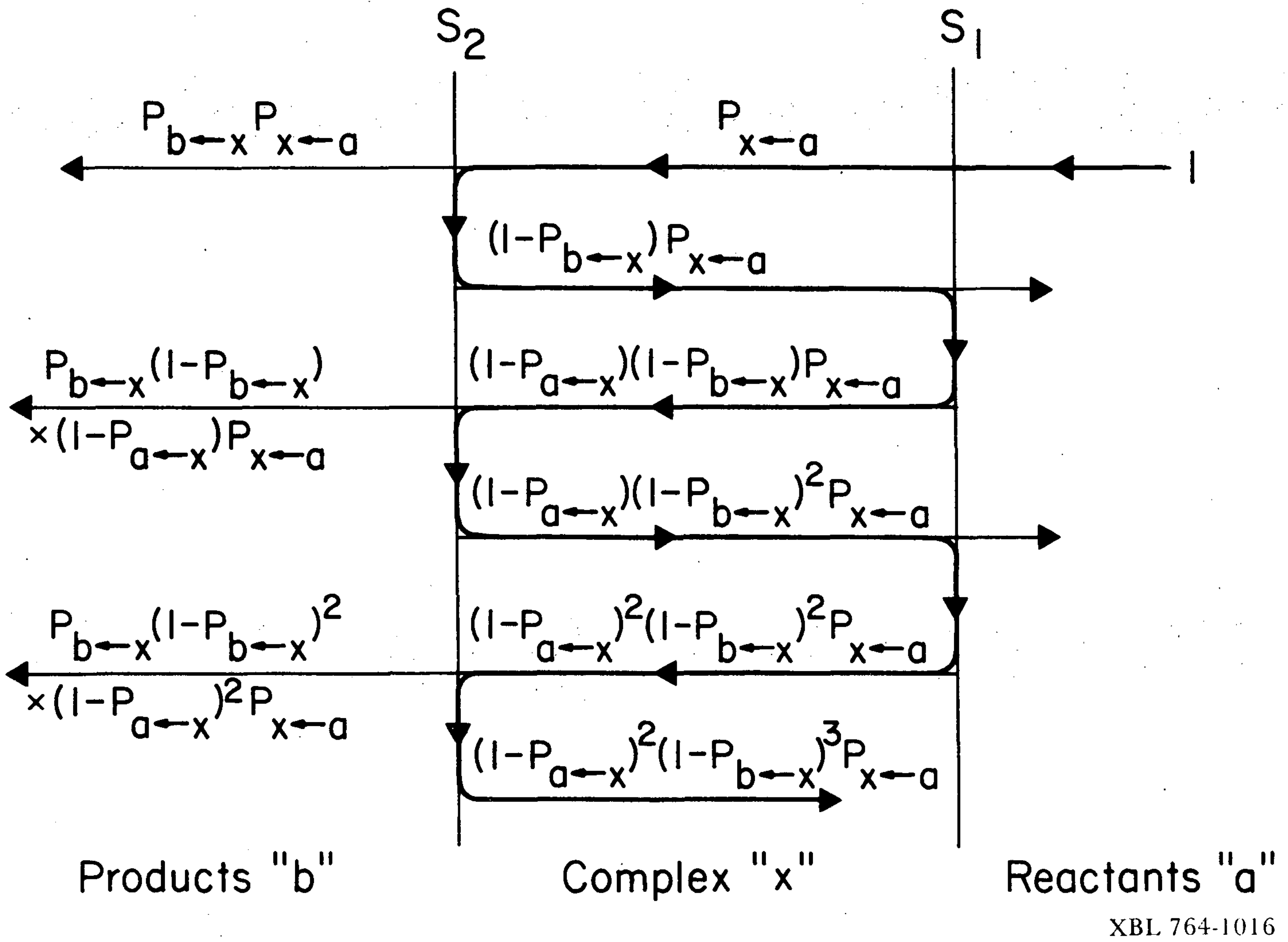
S_2
S_1
$P_{b \leftarrow x} P_{x \leftarrow a}$
$P_{x \leftarrow a}$
1
$(1-P_{b \leftarrow x}) P_{x \leftarrow a}$
$P_{b \leftarrow x}(1-P_{b \leftarrow x})$
$\times (1-P_{a \leftarrow x}) P_{x \leftarrow a}$
$(1-P_{a \leftarrow x})(1-P_{b \leftarrow x}) P_{x \leftarrow a}$
$(1-P_{a \leftarrow x})(1-P_{b \leftarrow x})^2 P_{x \leftarrow a}$
$P_{b \leftarrow x}(1-P_{b \leftarrow x})^2$
$\times (1-P_{a \leftarrow x})^2 P_{x \leftarrow a}$
$(1-P_{a \leftarrow x})^2(1-P_{b \leftarrow x})^2 P_{x \leftarrow a}$
$(1-P_{a \leftarrow x})^2(1-P_{b \leftarrow x})^3 P_{x \leftarrow a}$
Products "b"
Complex "x"
Reactants "a"
XBL 764-1016

Figure 3

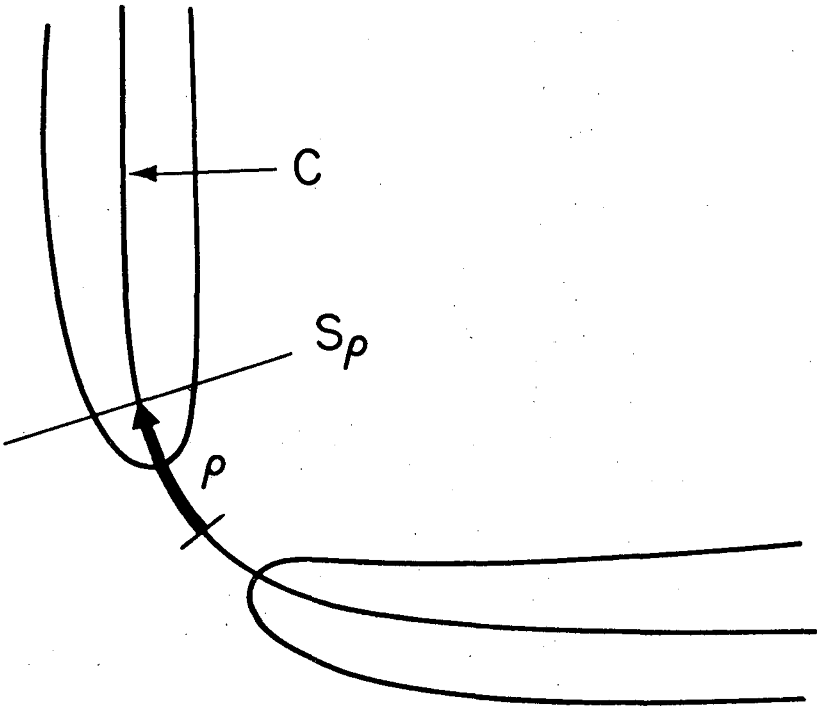

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Figure 4

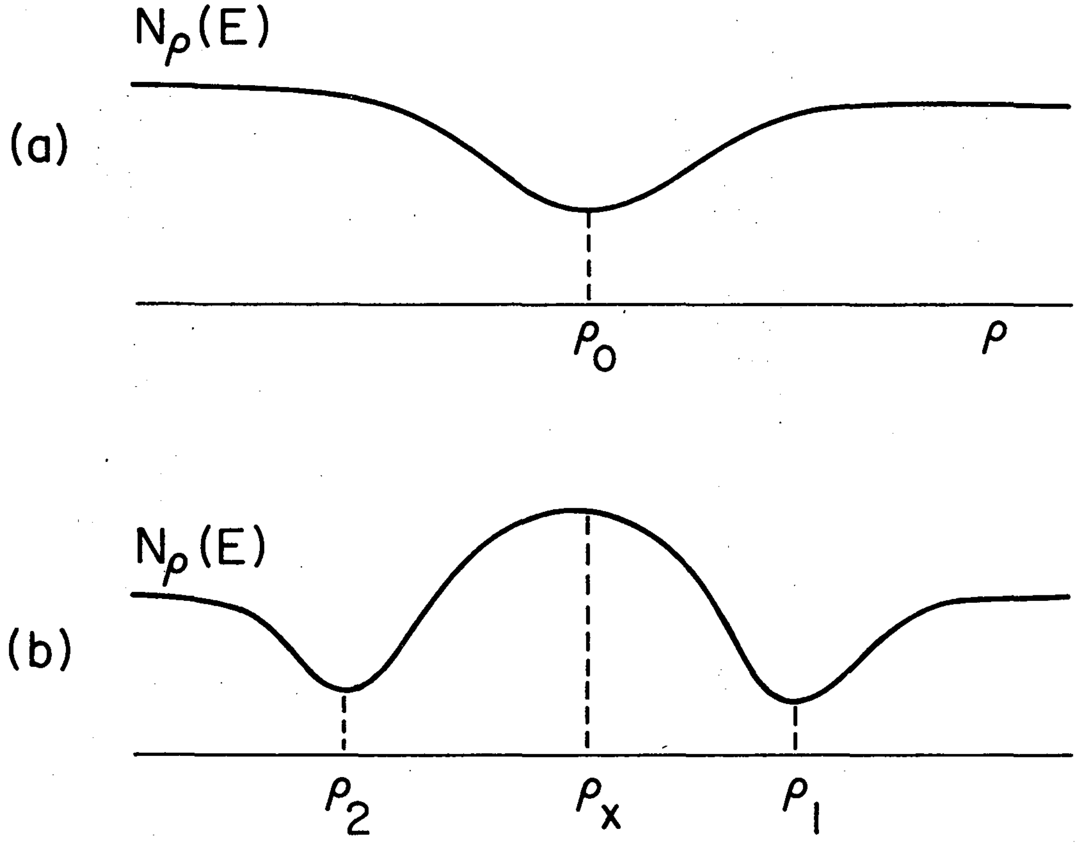

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Figure 5

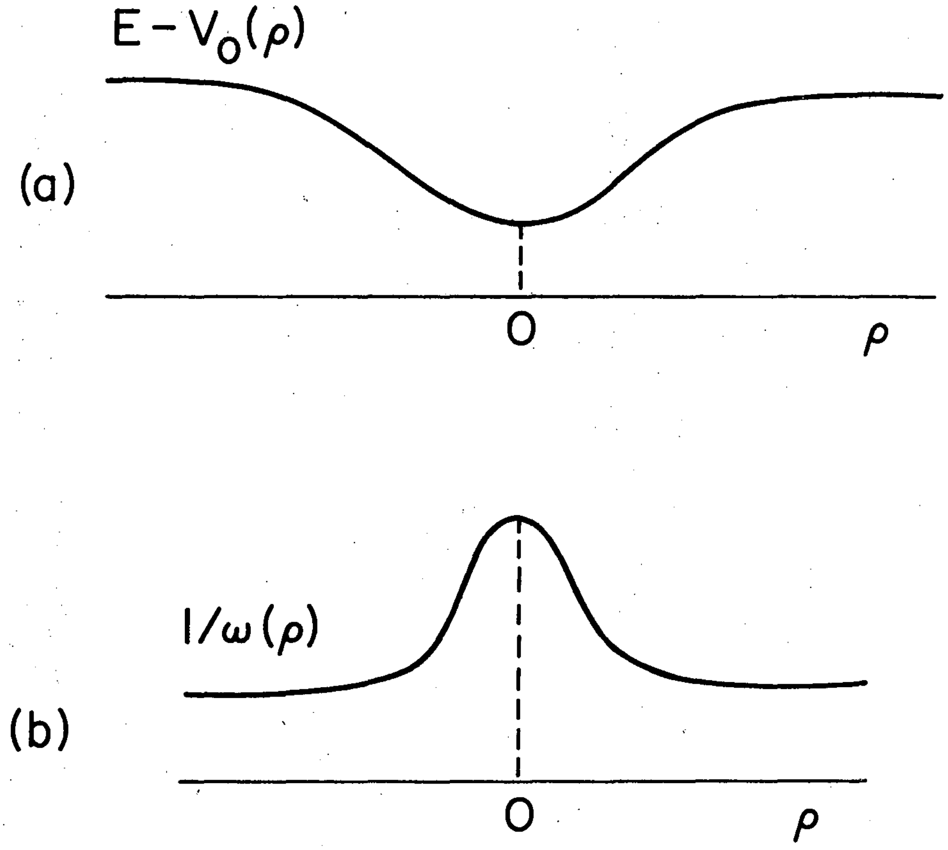

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Figure 6

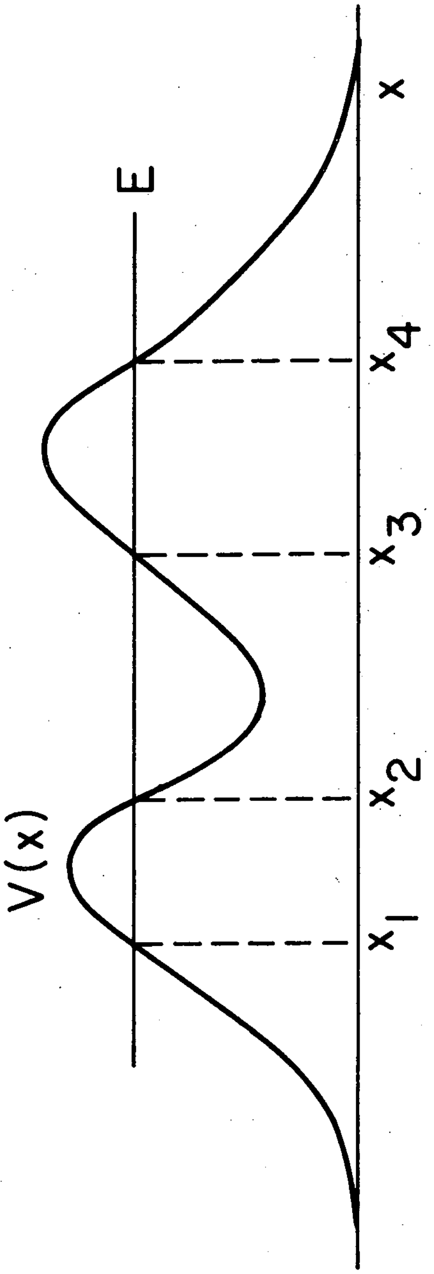

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Figure 7

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