

normal two-electron chemical bond,²⁵ consistent with activation energies for simple bond break assumed in this paper.

CONCLUSIONS

While the assignments of frequencies and activation energies are in many ways arbitrary, we feel that the agreement shown here indicates the validity of a statistical approach to mass spectra. There would certainly be no problem in fitting all the photoioniza-

²⁵ L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Co., Inc., New York, 1935), pp. 362-363.

tion data of Steiner, Geise, and Inghram within the framework of the general formulation of the quasiequilibrium theory, as defined by Eq. (1), if one were to postulate multiple-reaction mechanisms involving varied potential surfaces for different electronic states. Such calculations would be meaningless because the lack of data would permit an essentially complete freedom of choice of the parameters associated with such a general model. Thus, a significant test of the validity of the theory will require further data such as might be obtained by the experiments described in their discussion by Steiner *et al.* and by other experiments which will give a more direct indication of the rate of energy randomization.

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Chemical-Reaction Cross Sections, Quasiequilibrium, and Generalized Activated Complexes*

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A quasiequilibrium expression is given relating sums over reaction cross sections to properties of activated complexes. When applied to recent classical-mechanical computer data on the H+H₂ reaction to test the quasiequilibrium assumption, reasonable agreement is found over the range considered. Suggestions are made with respect to extending the range and to presenting the computer data in a modified form. The latter would permit testing a stronger statement of the hypothesis. The equations are used elsewhere to formulate a statistical-dynamical theory for chemical-reaction cross sections.

INTRODUCTION

A QUASIEQUILIBRIUM hypothesis appears in a prominent way in the activated-complex theory of chemical reactions. This hypothesis, in a form appropriate to systems having specified constants of the motion, is used below to obtain equations involving sums over reaction cross sections. Curvilinear effects are not excluded.^{1,2}

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¹ (a) In the usual activated-complex theory a Cartesian reaction coordinate is used for simplicity, an assumption which has certain consequences for the kinetic-energy operator and for the computation of the transmission coefficient. (b) Curvilinear effects for transmission coefficients were first considered by H. M. Hulbert and J. O. Hirschfelder [*J. Chem. Phys.* **11**, 276 (1943)] and by D. W. Jepsen and J. O. Hirschfelder [*ibid.* **30**, 1032 (1959)]. They employed discontinuous potential-energy surfaces. (c) L. Hofacker has formally included curvilinear effects in his discussion of reaction-rate theory for smooth surfaces, *Z. Naturforsch.* **18a**, 607 (1963).

² (a) Equations for an activated-complex theory for curvilinear coordinate systems and smooth potential-energy surfaces were derived in R. A. Marcus, *J. Chem. Phys.* **43**, 1598 (1965) [cf. *ibid.* **41**, 2614, 2624 (1964)]; we utilize these results and their extension in Ref. 2(c). (b) R. A. Marcus, *ibid.* **41**, 603 (1964), Table I. Some further examination of these results is desirable for curvilinearity derived in Ref. 2(c). (c) R. A. Marcus (to be published).

The results are compared with a recent extensive computer integration of the classical-mechanical equations of motion^{3a} for the H+H₂ reaction. They are found to be in reasonable agreement with the latter without use of adjustable parameters. Previously, computer calculations of collinear collisions, quantum^{3b} and classical,^{3a} were compared² with activated-complex theory in the same vibrational adiabatic hypothesis used for analyzing the data here and found to be in agreement with those simpler calculations also.

In the present paper, the comparison with electronic computer results involves sums over cross sections for all states of the same total energy. A comparison with cross sections of individual states requires additional analysis and is given in a later paper (Part II of a series on reaction-cross-section theory).

Recommendations are made for obtaining additional data and for presenting the old data in a modified form so as to permit other tests. Comparison with a rate-

³ (a) F. T. Wall, L. A. Hiller, Jr., and J. Mazur, *J. Chem. Phys.* **29**, 255 (1958) and subsequent papers; (b) E. M. Mortensen and K. S. Pitzer, *Chem. Soc. (London) Spec. Publ.* **16**, 57 (1962); (c) M. Karplus, R. N. Porter, and R. D. Sharma, *J. Chem. Phys.* **43**, 3259 (1965).

constant test^{3a} is also made. Finally, the expressions are used elsewhere to formulate a theory of chemical-reaction cross sections.

QUASIEQUILIBRIUM

During a collision the energy E , the total angular-momentum quantum number J and its component along some axis M are conserved. In terms of the activated complex concept a quasiequilibrium hypothesis can be phrased as follows. When all quantum states of a reacting pair having a given J , M and a total energy within $(E, E+dE)$ are made equally likely, all quantum states in the activated-complex region having this J , M , and $(E, E+dE)$ are also equally likely, each occurring with the same probability as those of the pair.⁴

When some other quantum number (or classical action variable) v is also conserved, a sharper form of this quasiequilibrium hypothesis is obtained by replacing " J and M " by " J , M , and v ." As an example there is the case where v refers to a particular vibrational coordinate in some three-center exchange reactions, $A+BC \rightarrow AB+C$.^{2c}

Equations based on the above hypothesis are obtained below. An ensemble of reacting pairs is first considered, uniformly distributed among all quantum states in the energy range $E, E+dE$. Later, subsets are considered, each having a particular J , a particular v , or both. Center-of-mass coordinates are used. The following list contains some of the additional notation used:

E_N	Energy of N th rotation-vibration quantum state of the reacting pair
μ	Reduced mass of reactants
p	Initial relative momentum of reactants
k	Corresponding wavenumber, p/\hbar
\mathcal{F}	Probability flux of formation of products per unit time
σ_{Np}	Reaction cross section for a given N and p
v, E_v	Quantum number and energy of the adiabatic modes of the reacting pairs
l, m_l	Quantum numbers for the orbital angular momentum of the initial relative motion
\mathcal{N}	Number of translational-rotational-vibrational quantum states of a reacting pair in the range $(E, E+dE)$ when the pair is in a volume V . Later, the symbol \mathcal{N} is used for ensembles also having a given J , a given v , a given l , or some combination of these
Γ	An operator, $\sum \gamma$, where γ is the number of optical isomeric paths of any geometrical isomeric path, from reactants to activated complex, and where \sum represents summation over all geometric isomeric paths. ^{2a} Thus, Γ represents a summation over all

⁴ A related assumption for unimolecular reactions was made by R. A. Marcus and O. K. Rice, *J. Phys. Colloid Chem.* **55**, 894 (1951); R. A. Marcus, *J. Chem. Phys.* **20**, 359 (1952); **43**, 2658 (1965). There, a quasiequilibrium between energetic ("active") molecules A^* and activated complexes A^\ddagger of the same E and J was assumed.

optical and geometric isomeric paths from reactants to activated complex.

DERIVATION OF EQUATIONS

The number of translational quantum states of a reacting pair is $4\pi p^2 dp V/h^3$, when p lies in $(p, p+dp)$ and the volume of the system is V ,⁴ the numerator being the corresponding six-dimensional phase-space volume element. The probability of finding the reacting pair in one of these states and, at the same time, in some accessible rotation-vibration quantum state N is $4\pi p^2 dp V/h^3 \mathcal{N}$. When a reacting pair is definitely in one of these quantum states, it is in the volume V and has an incident translational wavefunction, $V^{-1/2} \exp(i\mathbf{k} \cdot \mathbf{r})$, normalized to the volume V .

The total probability flux of such incident reacting pairs (number per area per time) is the velocity p/μ multiplied by V^{-1} , the probability of finding the pair in a unit volume, and multiplied by the chance of finding the pair in these states, $4\pi p^2 dp V/h^3 \mathcal{N}$, i.e., it is $4\pi p^3 dp/\mu h^3 \mathcal{N}$. The contribution of these states to the probability flux of the products \mathcal{F} (number per time) is therefore, by definition, equal to this quantity multiplied by the reaction cross section σ_{Np} . The total flux \mathcal{F} is obtained by summing over all states N consistent with the total energy lying in $(E, E+dE)$:

$$\mathcal{F} = \sum_N 4\pi p^3 dp \frac{\sigma_{Np}}{\mu h^3 \mathcal{N}} \quad (1)$$

On the other hand, if q^r is the reaction coordinate and p_r is its conjugate momentum, the probability of the reacting pair being in the phase-space volume element $dq^r dp_r$, and in a rotation-vibration quantum state N^+ of the activated complex is $dq^r dp_r/h^3 \mathcal{N}$ by the quasiequilibrium hypothesis. This probability per unit q^r is obtained by dividing by dq^r . The net flow \mathcal{F} through a q^r -coordinate hypersurface S just outside the activated-complex region is obtained^{5a} by multiplication by $P_{N^+} dS$ (the

⁵ (a) These arguments were also used^{2a} to derive an expression for the rate. (b) When the q^r -coordinate curves are made orthogonal to the rest, q^r equals $g^{rr} p_r$ and (q^r) equals $(g^{rr}) p_r$, where g^{rr} is a coefficient in the kinetic-energy expression. As shown in Ref. 2(a), $(g^{rr}) p_r dp_r$ equals dE when the system remains in the given state N^+ on going from S through the activated-complex region.

When the q^r motion is treated classically throughout that region, S may be chosen to coincide with the q^r -coordinate hypersurface constituting the activated complex ($q^r = q^{r*}$). Then, the condition of remaining in State N^+ during motion through the activated-complex region is automatically fulfilled, since that "region" now collapses to a hypersurface $q^r = q^{r*}$. When the q^r motion in the vicinity of $q^r = q^{r*}$ is treated quantum mechanically, however, the condition of remaining in the same state N^+ is fulfilled only in some approximation such as the adiabatic, separable, or separable-adiabatic approximation discussed in Ref. 2(a) and in much more detail in Ref. 2(c).

From a dynamical point of view, the quasiequilibrium hypothesis is perhaps best fulfilled the closer S is to the reacting pair's region of configuration space, while the chance of remaining in the same state N^+ on going through the activated-complex region is best fulfilled the closer S is to that region. When diffraction effects along q^r occur, they should do so most in the activated-complex region, for there the wavenumber for the q^r motion is least.^{2a} Thus, S in this quantum treatment of the q^r motion cannot be taken too close to the activated complex's q^r -coordinate hypersurface.

relative probability of passing through an area element of S , dS , in the given state N^+ , by the velocity component q^r at that dS , and by the transmission coefficient $\kappa(E, N^+)$, and finally by integration over all of S and by summation over all N^+ for which the total energy does not exceed E :

$$\mathcal{F} = \sum_{N^+} \langle \dot{q}^r \rangle d p_r \kappa(E, N^+) / h \mathcal{N}, \quad (2)$$

where $\langle \dot{q}^r \rangle$ is $\int \dot{q}^r P_{N^+} dS$.

However, there may also be several different reaction paths from reactants to activated complexes.^{2a} Paths which are optical isomers of each other will have similar dynamical properties, e.g., similar $\kappa(E, N^+)$'s. Paths which are geometric isomers^{2a} of each other differ somewhat in their properties. We include all paths by introducing into (2) the operator Γ defined earlier.

Upon equating (1) and this modified (2), noting that dE equals $\dot{p}d\dot{p}/\mu$ and also^{5b} equals $\langle \dot{q}^r \rangle d p_r$, and finally setting \dot{p} equal to $k\hbar$, Eq. (3) is obtained^{6a}:

$$\sum_N (k^2/\pi) \sigma_{Np} = \Gamma \sum_{N^+} \kappa(E, N^+). \quad (3)$$

If a more restricted ensemble than that used above is considered, namely one where each reacting pair is in a state v for the adiabatic coordinates, the quantum number N denotes a set (n, v) and N^+ denotes a set (n^+, v) . Here, the quantum number n refers to all rotational-vibration degrees of freedom of the pair reactants, exclusive of the adiabatic degrees of freedom, and n^+ refers to those of the activated complex. In this case, Eq. (3) is again obtained, but with the sums over N and N^+ replaced by sums over n and n^+ ,

$$\sum_n (k^2/\pi) \sigma_{vnp} = \Gamma \sum_{n^+} \kappa(E, v, n^+). \quad (4)$$

If, instead, each reacting pair in the ensemble is made to have a given total angular momentum quantum number J (orbital plus rotational included), only certain orbital angular momenta can be selected for each rotational angular momentum state. The counterpart of (3) or (4) can be expressed in terms of reaction probabilities, w_{lNp}^J , where N includes the rotational quantum number j . Here, the w_{lNp}^J is the probability that a reacting pair with quantum numbers l and N prepared in the state JM will react. Instead of (3) one

⁶ (a) Expressions for rate constants of restricted ensembles in terms of reaction cross sections are given by M. A. Eliason and J. O. Hirschfelder, *J. Chem. Phys.* **30**, 1426 (1959), and by J. Ross and P. Mazur, *ibid.* **35**, 19 (1961). Such expressions, in conjunction with curvilinear activated-complex equations derivable^{2a} for such ensembles, could be used to derive Eq. (3) in an alternate way, when the technique of Laplace transform is used. However, for our purposes, such an alternative derivation of (3) or (4) would be a roundabout one. (b) See also Eliason and Hirschfelder in Ref. 6(a), who derive an activated-complex theory type of equation for the rate constant, assuming an adiabaticity for all coordinates (excluding the reaction coordinate) throughout the motion.

obtains, as in Appendix I,

$$\sum_N \sum_{l=|J-j|}^{J+j} w_{lNp}^J = \Gamma \sum_{N^+} \kappa(E, N^+). \quad (5)$$

The sums over N and N^+ are restricted so as to be consistent with the given J , M , and E .

For a given v and J we obtain (6) instead, where the sums over n and n^+ are restricted so as to be consistent with this J , M , E , and v :

$$\sum_n \sum_{l=|J-j|}^{J+j} w_{lvnp}^J = \Gamma \sum_{n^+} \kappa(E, v, n^+). \quad (6)$$

The probability of reaction of a reacting pair prepared in a state lNp is given by (7)⁷; the reaction cross section is given by (8)⁸:

$$w_{lNp} = \sum_{J=|l-j|}^{l+j} (2J+1) \frac{w_{lNp}^J}{(2j+1)(2l+1)}, \quad (7)$$

$$\sigma_{Np} = (\pi/k^2) \sum_{l=0}^{\infty} (2l+1) w_{lNp}. \quad (8)$$

ADDITIONAL POSTULATES

A variety of additional assumptions may be superimposed on Eqs. (3) to (6). Some possible assumptions for the motion in the vicinity of the activated complex are listed below:

(1) The q^r motion is Cartesian. In this case κ depends only on the energy of the q^r motion. There are no coupling terms between q^r and the other coordinates when q^r is Cartesian.

(2) The q^r motion is curvilinear but classical. In this case $\kappa(E, N^+) = 0$ when $E < \epsilon_{N^+}$ and $\kappa(E, N^+) = 1$ when $E \geq \epsilon_{N^+}$, where ϵ_{N^+} is some energy determined by the mechanics.^{2a, 6b} The right-hand sides of (3) to (6) then become sums over all states of the activated complex for which $\epsilon_{N^+} \leq E$ for the given E , given E and v , given E and J , or given E and J and v , respectively. The ϵ_{N^+} needed for a count of the number of accessible states, $\sum_{N^+} 1$, in this classical case is the ϵ_{N^+} for $q^r = q^{r^*}$ and $q^r = 0$.

(3) The q^r motion is both Cartesian and classical. In this Cartesian case the total energy in the vicinity of the activated complex is the sum of two contributions, one being the kinetic energy plus $V(q^r)$, the potential energy for the q^r motion, the other containing the energy for the other coordinates, E_{N^+} . Then,

⁷ There are $(2l+1)(2j+1)$ states of given l and j , for given values of the remaining quantum numbers. Of these states $2J+1$ have the value J , when J lies in the interval $|j-l|$ to $j+l$. Equation (7) then follows.

⁸ For example, L. D. Landau and E. M. Lifschitz, *Quantum Mechanics* (Addison-Wesley Publ. Co., Inc., Reading, Mass., 1958), p. 437.

$\epsilon_{N^+} = E_{N^+} + V_0$, where V_0 is the value of $V(q^r)$ when q^r has the value q^{r+} appropriate to the activated complex.

(4) The q^r motion is the same as in No. 3, but the energy term ϵ_{N^+} is a sum of uncoupled adiabatic and nonadiabatic contributions, $\epsilon_{N^+} = E_{v^+} + E_{n^+} + V_0$.

(5) The q^r motion is curvilinear, nonclassical, and, near the activated complex, separable, adiabatic, or separable-adiabatic.^{2a} The problem of determining $\kappa(E, N^+)$ was discussed briefly in Ref. 2(a) and in much more dynamical detail in Ref. 2(c).

CLASSICAL-MECHANICAL RESULTS

The sums in the preceding equations involve sums over points in a multidimensional quantum number space, i.e., in a space where the coordinates are quantum numbers. To achieve the corresponding classical results, the sums are replaced by integrals, the quantum numbers then becoming continuous variables. The expressions still contain Planck's constant. However, when feasible, one can introduce classical action variables⁹ J_i ($J_i = \oint p_i dq_i$ for the i th periodic coordinate), use the Bohr-Sommerfeld rule $J_i = n_i h$, convert the integration from one over a space of n_i coordinates to one over a space of J_i coordinates. Since the dimensionality of the integration space on the right-hand sides of Eqs. (3) and (4) is twofold less than that on the corresponding left-hand sides in each case, the h factor is found to cancel and so disappear in the classical version of these equations. A similar change of variable in (5) to (8) reveals the absence of an h factor in the classical limit there also, as expected.

ACTIVATED COMPLEXES

When the potential-energy surface is known, the choice of activated complex in the literature is quite standard in two well-known cases: (1) the saddle point of the surface is very pronounced, or (2) only long-range attractive and centrifugal forces need be considered. The $H+H_2$ reaction, discussed subsequently, is an example of Case (1).

For intermediate cases, as well as in the above ones, one can use instead a criterion stemming from the locally adiabatic, separable, or separable-adiabatic approximation used to derive Eqs. (3) to (6). It can be phrased simply in the following way for the adiabatic approximation, as one can see from Ref. 2(a) or 6(b).¹⁰

If ϵ_{N^+} denotes the total energy except for the kinetic energy of the reaction coordinate, choose that q^r for

⁹ For use of the angle-action variables in classical-mechanical problems see, for example, D. Ter Haar, *Elements of Hamiltonian Mechanics* (North-Holland Publ. Co., Amsterdam, 1961).

¹⁰ In Refs. 2(a) and 6(b) the same definition of q^{r+} is used. The two adiabatic treatments differ in the following respect: the one^{2a} assumes local adiabaticity (i.e., for q^r near q^{r+}) and the other^{6b} assumes adiabaticity in the large (i.e., for all q^r from $-\infty$ to q^{r+}). In Ref. 2(a), ϵ_{N^+} was called ϵ_k . Hofacker, in Ref. 1(c), also assumes adiabaticity in the large and appears to have a similar definition of q^{r+} .

which $\partial \epsilon_{N^+}(q^r)/\partial q^r$ vanishes. Such a q^r may be a function of N^+ , though in Case (1) above only to a negligible extent if the saddle point is sufficiently pronounced, but in Case (2) very strongly so, since N^+ includes the angular-momentum quantum number. In intermediate cases, where the frequencies of the newly formed bending vibrations are appreciably dependent on q^r , the value of q^{r+} thus calculated also depends on their quantum number for it too is present in N^+ .

For the separable or separable-adiabatic approximations, q^{r+} is defined in a slightly different way^{5,11} because of curvilinear effects.

These criteria reduce to the standard ones for Cases (1) and (2) above, when the explicit conditions appropriate to those cases are introduced.

REMARKS ON ADIABATIC COORDINATES

When Eq. (4) is used rather than Eq. (3) some prescription is needed for the adiabatic modes held in State v . If any internal vibrational modes inside Groups A or B or C in $A+BC \rightarrow AB+C$ are only weakly coupled to the reaction site, these modes should be adiabatic if the collision complexes are sufficiently short lived. Again, if the BC molecule rotates freely in the activated complex ("loose complex"), its rotational modes are adiabatic. In reactions involving an appreciable activation energy, however, the rotation of BC is expected to be restricted. In this case, an examination of potential-energy contour plots for the reaction indicates that the "symmetric" stretching mode $A \rightarrow B - C$ in linear or near-linear activated complexes is adiabatic, with or without nonadiabatic corrections.¹¹

In a dynamical analysis of the latter situation, given in a later paper,^{2c} an approximate nonadiabatic correction term to ϵ_{N^+} is obtained, applicable to both Eqs. (3) and (4). When the nonadiabatic corrections are severe, and not random, the formalism of activated-complex theory should break down, and with it Eqs. (3) and (4). Such corrections can occur when the system is moving extremely rapidly in a critical region of the reaction coordinate curve, a region where the reaction path is appreciably curved in a center-of-mass, skewed-axes¹² space, and when, at the same time, that region coincides with or precedes the activated-complex region.

¹¹ For example, in the separable approximation in Ref. 2(a) one finds there that the function

$$\sum_{\nu=1}^m \alpha_{\nu} \phi_{\nu}(q^r) - X_r(q^r)$$

and its derivative with respect to q^r (at fixed α_{ν} 's) should be set equal to zero in order to find q^{r+} and ϵ_{N^+} . Here, α_1 is ϵ_{N^+} , ϕ_{ν} , α_{ν} , and X_r are defined there. For a given N^+ and α_1 , all remaining α_{ν} are known. Thus, with the above two equations, q^{r+} and all α_{ν} ($\nu=1$ to m) can be found. In Ref. 2(a), ϵ_{N^+} was called ϵ_k .

¹² S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Co., Inc., New York, 1941), p. 102.

APPLICATION TO H+H₂ REACTION

Some extensive and highly informative numerical integrations have been made for the classical-mechanical equations of motion for this reaction.³ Reaction cross sections⁵⁰ were calculated for states where the hydrogen molecule had its zero-point energy and had a rotational energy numerically equal to $j(j+1)\hbar^2/2I$, $j=0, 1, \dots, 5$. The initial relative velocity V_R was varied from 0.9×10^6 to 2.0×10^6 cm sec⁻¹.

To test Eq. (3), cross sections for a range of vibrational energies of H₂ are needed. However, cross sections for only one vibrational state are needed to test Eq. (4) when the reaction is adiabatic for this vibration. As noted in the preceding section and based also on an analysis of computer results on collinear collisions for this reaction,² we assume the reaction to be adiabatic with respect to a particular vibration, the one which is the vibration of H₂ in the reacting pair and which becomes the H₃ symmetric stretch in the activated complex.

To test Eq. (4) it is further required that the cross sections in the classical-mechanical case be given for a continuous range of j 's, rather than for just a discrete set. For this reason, it is necessary to interpolate the data of Ref. 3(c) to evaluate the desired integral. Further, we superimpose on Eq. (4) the approximation No. 4 mentioned earlier: classical and Cartesian q^r and additivity of E_v^+ and E_{n^+} . At high energies, higher than those used here, it may be necessary to use approximation No. 2 instead of 4, i.e., to use a curvilinear rather than a Cartesian q^r , in a form described in Refs. 2(c) and 14. However, the computer data for the high j 's needed to test Eq. (4) at high energies have not yet been published.

With the above approximation Eq. (4) can be shown to become

$$\sum_n (k^2/\pi) \sigma_{vnp} = \Gamma \sum_{n^+} 1. \quad (9)$$

For this H+H₂ reaction, the quantum number n denotes j and its component m_j , while n^+ denotes the rotational quantum number J , its component M , and the bending vibrational quantum numbers v_2 and K_2 , where K_2 goes from $-v_2$ to v_2 in steps of 2.¹³ The energy of the activated complex depends on v_2 and on J .^{13a} Since σ_{vijp} is independent of m_j , we obtain

$$\sum_j (k^2/\pi) (2j+1) \sigma_{vijp} = \Gamma \sum_J (2J+1) \sum_{v_2} (v_2+1), \quad (10)$$

¹³ (a) Rotation-vibration interaction and vibrational angular-momentum terms are neglected, for example. The energy depends slightly on K_2 even in that case, when the bending oscillators are anharmonic.¹⁴ (b) For example, G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Co., Inc., Princeton, N.J., 1945).

¹⁴ At higher energies one should use an anharmonic correction for E_{v_2} . [Compare a forthcoming publication of the author on reaction cross sections, Part II: R. A. Marcus, *J. Chem. Phys.* (to be published).]

where the sums are over all quantum numbers consistent with the total energy of the system not exceeding E .

Since the σ_{vijp} were computed classically in Ref. 3(c), the purely classical version of (10) should be used to test the quasiequilibrium assumption. Adiabaticity means, in classical mechanics, constancy of the action variable for this coordinate. For a harmonic vibration of initial frequency ν and of frequency ν^+ in the activated complex, the action^{9,2a} is E_v^+/ν^+ , respectively. That is, $E_v/\nu = E_v^+/\nu^+$. Thus, E_v^+ equals $E_v\nu^+/\nu$. When E_v is made numerically equal to $h\nu/2$, as in Ref. 3(c), E_v^+ equals $h\nu^+/2$, which is 3.12 kcal mole⁻¹ in the present case.

The purely classical counterpart of (10) is (11), where the action variables \mathbf{j} , \mathbf{J} , and \mathbf{v}_2 correspond to (though do not exactly equal) $j\hbar$, $J\hbar$, and $v_2\hbar$, respectively, and where σ and σ^+ are symmetry numbers of H₂ and of the activated complex H₃, respectively. We also use the fact that E equals $E_p + E_j + E_v$, where E_p is the initial translational energy ($p^2/2\mu$) in the center-of-mass system and E_j is the rotational energy, $j^2/8\pi^2I$:

$$\frac{8\pi\mu}{\sigma} \int_{j=0}^{j^{\max}} (E - E_v - E_j) \sigma_{vijp} 2j dj = \Gamma \int_{J=0}^{J^{\max}} \frac{2J}{\sigma^+} \left(\int_{v_2=0}^{v_2^{\max}} v_2 dv_2 \right) dJ. \quad (11)$$

The maximum value of v_2 , v_2^{\max} is that for which the bending vibrational energy equals the maximum available energy $E - V_0 - E_v^+ - E_j^+$. Here, E_j^+ equals $J^2/8\pi^2I^+$. The maximum values of \mathbf{j} and of \mathbf{J} are those for which E_j equals $E - E_v$ and for which E_j^+ equals $E - V_0 - E_v^+$, respectively.

To avoid introducing a harmonic approximation for the bending vibrations until the final step, the order of integration in the right-hand side of (11) is interchanged¹⁵ and the latter integrated to yield $8\pi^2I^+ \times \int (E - V_0 - E_v^+ - E_{v_2^+}) v_2 dv_2$, where v_2 goes now from 0 to the value for which $E_{v_2^+}$ equals $E - V_0 - E_v^+$. Further, in the left-hand side of (11) the integration can be written as one over E_j . We obtain

$$\int_{E_j=0}^{E-E_v} (E - E_v - E_j) \sigma_{vijp} dE_j = \frac{\Gamma I^+ \sigma}{8\pi I \sigma \mu} \int_{v_2=0}^{v_2^{\max}} (E - V_0 - E_v^+ - E_{v_2^+}) v_2 dv_2. \quad (12)$$

When a harmonic approximation¹⁴ is introduced for $E_{v_2^+}$, (12) becomes (13), where v_2 is the bending

¹⁵ Then, E_j^+ goes from 0 to $E - V_0 - E_v^+ - E_{v_2^+}$, where $E_{v_2^+}$ is the energy of the bending modes when the action is v_2 .

frequency

$$\int_{E_j=0}^{E-E_v} (E-E_v-E_j)\sigma_{vij}dE_j = \frac{\Gamma(E-V_0-E_v^+)^3\sigma I^+}{48\pi\sigma^+I\mu\nu^2} \quad (13)$$

For the range of j 's investigated in the computer study E_j was varied from 0 to 5.25 kcal mole⁻¹.¹⁶ E_v was 6.20 kcal mole⁻¹.³⁰ The sum σ_{vij} of the cross sections for $A+BC\rightarrow AB+C$ and $A+BC\rightarrow AC+B$ was plotted and tabulated in Ref. 3(c). The numerical data given there suffice for evaluating the integral in the left side of (13) for an interval of E 's from about 15 to 19 kcal mole⁻¹. (At lower E 's the published number of E_j points is too small.) Using the results given in Ref. 3(c), with energies in kilocalories per mole and with σ_{vij} in atomic units (a.u.), the left-hand side of (13) was estimated to be about 9.6, 24.5, and 55 when E was 15.5, 17.0, and 18.5 kcal mole⁻¹, respectively. The error in these figures, arising from interpolation, from extrapolation, and from the existing scattering of points in Ref. 3(c), is of the order of 5% to 10%.

In the σ_{vij} describing the above reaction pair, there are three distinguishable atoms, A, B, and C, so that σ and σ^+ both equal unity. There are two reaction paths, each being the geometric isomer of the other, so $\Gamma=2$. [Had σ_{vij} been calculated only for $A+BC\rightarrow AB+C$ in Ref. 3(c), there would have been only one geometric isomeric path involved, and so Γ would have been unity.] $V_0+E_v^+$ is 12.25 kcal mole⁻¹, since V_0 is 9.13 and E_v^+ is 3.12. The right-hand side of (13) becomes 0.202 $(E-12.25)^3$ (kcal mole⁻¹)² a.u., where E is in kilocalories per mole. The right-hand side of (13) is thus found to be 7.0, 22, and 50 when E is 15.5, 17.0, and 18.5 kcal mole⁻¹, respectively, in good agreement with the computer values cited above.

At very high energies anharmonic formulas,¹⁴ with nonadiabatic corrections²⁰ perhaps, should be used, yielding thereby a modified form of (13). An anharmonic correction for the bending vibrations is estimated elsewhere.¹⁴

COMPARISON WITH AN ALTERNATIVE TEST

Another way of testing the quasiequilibrium assumption is to compare certain computer-calculated rate constants with those based on activated-complex theory. There is a Laplace transform relationship⁶ between rate constants for ensembles of specified N or n and ν and reaction cross sections. When effected over an infinite temperature range, such an alternative test is mathematically equivalent to the testing of Eqs. (3) and (4) over an infinite energy range, when generalized activated complexes are used. It is not equivalent to

the testing of (5), because of the additional partitioning among the J 's in the latter.

The test based on rate constants involves one more integration, however, thereby making anharmonic and (perhaps) curvilinear corrections more difficult. Again, it cannot reveal as sharply the energy range where deviations from the quasiequilibrium hypothesis might begin to occur, since it involves averaging over a range of thermal energies. Nevertheless, the alternative test is especially useful for answering very directly a question of major importance, namely how accurate activated-complex theory is for calculating rate constants.

A test of this alternative type was made in Ref. 3(c) over a temperature range from 300° to 1000°K. Standard activated-complex theory was used, and so the reaction coordinate was Cartesian. The agreement at 1000°K was excellent (about 20%), but at lower temperatures the agreement became progressively poorer, the results differing by a factor of 6 at 300°K. Yet, the energy range in this test overlaps that in the present one: in the former the average energy of the classical activated complexes in the center-of-mass system is $V_0+E_v^++4RT$. ($2RT$ arises from the two bending modes of H_3 , RT from the two rotations, and RT from the kT/h factor, i.e., from the translation along the reaction coordinate.) When T is varied from 300° to 1000°K this average energy is varied from 14.7 to 20.3 kcal mole⁻¹, overlapping the range in this paper.

The source of the disagreement in the rate-constant test as used in Ref. 3(c), in the contrast with the good agreement of the above test of Eq. (4) in the same energy range, appears to be at least in part due to the use of a hybrid procedure there,³⁰ instead of using purely classical calculations throughout. A quantum distribution of initial states was combined with computer-calculated classical reaction cross sections, to calculate a quantum rate constant, which was compared with an activated-complex expression containing a quantum-mechanical partition function for the bending modes. (Had the latter been classical, as it was at 1000°K, the agreement would have been better.) Classical comparisons are now in progress.³⁰

Quantum-mechanical computer calculations of chemical reaction cross sections are also of particular interest of course, and not only for comparison with experiment. Those calculations will reveal whether the quantization of bending mode quantum states is realized during the collision. If these quantum states are formed, the present good agreement between the classical form of Eq. (4) and the classical computer results in a particular energy range has a hopeful consequence: Eqs. (3) to (5) may agree with data based on quantum-mechanical computer-calculated reaction cross sections in this energy range.

However, there is no *a priori* reason to presume with confidence that these bending vibration stationary states will be formed.

¹⁶ E_j was 0, 2, 6, 12, and 20, in units of $\hbar^2/2I$.

FURTHER EXTENSIONS OF DATA

It would also be desirable to test the quasiequilibrium assumption without resorting to the vibrational adiabatic hypothesis, i.e., to test Eq. (3). For this purpose reaction cross-sections are needed for all vibrational energies in the range of interest, rather than for just one. The adiabatic approximation is not a perfect approximation, and some breakdown of it would be expected. Indeed, extremely small cross sections ($\sim 0.005a_0^2$) were detected at low energies where the activated complex could not have had an energy $h\nu^+/2$ in the adiabatic mode. This small residual reaction rate might well be termed the "nonadiabatic leak."

It would also be desirable to extend the test of Eqs. (2) and (3) to higher energies. For purposes of testing the equations at these higher energies, computer data at higher rotational energies would be needed.

Then again, it would be desirable to test the quasiequilibrium hypothesis in a more stringent way by presenting computer data in the form of w_{lNp}^J 's as well as σ_{Np} 's. Such tests of Eqs. (5) and (6) would have a variety of consequences, some of which are discussed elsewhere.

APPENDIX: DERIVATION OF EQS. (5) AND (8)

For a given Np various orbital terms l can occur. We select those which, in conjunction with the j in N , give rise to a particular J . Such l 's must lie in the interval $|J-j|, \dots, J+j$.

In the ensemble described in the text the chance of finding the system in a particular $JMlNp$ state and in a given element $drdp$ of phase space is $drdp/h^3\Omega$, where r is the separation distance in the reacting pair. The probability per unit r is obtained by dividing by dr , and the contribution to the flux \mathcal{F}_J is then obtained by multiplying by the velocity \dot{r} and by w_{lNp} . Noting that $\dot{r}dp$ equals dE , summing over all l consistent with the j in N and with the energy not exceeding E one obtains (A1) for \mathcal{F}_J :

$$\mathcal{F}_J = \frac{dE}{h^3\Omega} \sum_N \sum_{l=|J-j|}^{J+j} w_{lNp}^J. \quad (\text{A1})$$

On equating this \mathcal{F}_J to the terms in (2) having this J Eq. (5) follows.

Equation (5) could also have been obtained by introducing into (1) the expression for σ_{Np} in terms of the w_{lNp}^J 's. The latter expression for σ_{Np} is given in Ref. 17. On then equating Eq. (1) for \mathcal{F} with (2), Eq. (5) follows,¹⁸ but summed over J , and with the order of summation interchanged. On interchanging the order of summation and, there being no cross terms between terms of different J 's in these transition probabilities, equating terms of the same J on both sides Eq. (5) is obtained.

Equation (8) is well known,⁸ but we use the present ensemble arguments to derive it, for completeness. To obtain (8) one can consider an ensemble of reacting pairs distributed uniformly over all states in the range $E, E+dE$. The probability of finding the system in a particular lNp state and in an element $drdp$ of phase space is $(2l+1)drdp/h^3\Omega$. Upon dividing by dr , multiplying by \dot{r} and by w_{lNp} the contribution of these states to \mathcal{F} is obtained. Summation over all l yields the contribution \mathcal{F}_N of states of given N :

$$\mathcal{F}_N = \frac{dE}{h^3\Omega} \sum_{l=0}^{\infty} (2l+1)w_{lNp}. \quad (\text{A2})$$

However, the argument preceding (A1) shows that \mathcal{F}_N is also the expression (A1) with the summation over N deleted. On equating these \mathcal{F}_N 's, Eq. (8) follows.

¹⁷ J. M. Blatt and L. C. Biedenharn, Rev. Mod. Phys. **24**, 258 (1952). With proper identification of symbols one obtains the following expression from their Eq. (4.12):

$$\sigma_{Np} = \frac{\pi}{k^2} \sum_{J=0}^{\infty} \sum_{l=|J-j|}^{J+j} \frac{(2J+1)}{(2j+1)} w_{lNp}^J.$$

¹⁸ The sum over N in Eq. (1) involves, among other things, sums over j and m_j . The σ_{Np} in the equation in Footnote 17 is independent of m_j . Summation over the m_j by summing over part of the N for a given j yields $2j+1$ equal terms, and so cancels the $1/(2j+1)$ factor.

For a given J the summation over N in Eq. (5) does not involve a sum over m_i , incidentally, since the m_j 's were used in conjunction with m_i 's to give various J 's and M 's for each j and l pair: There are $(2j+1)(2l+1)$ such combinations of m_j and m_l , and there are of course an equal number,

$$\sum_{j=|i-l|}^{J+i} (2J+1) = (2j+1)(2l+1),$$

of J, M pairs.