

ON THE QUANTUM MECHANICS OF CHEMICAL REACTIONS:
PREDISSOCIATION AND UNIMOLECULAR
DECOMPOSITIONSBY OSCAR KNEFLER RICE¹
UNIVERSITY OF CALIFORNIA, BERKELEY

(Received September 10, 1929)

ABSTRACT

In an ordinary chemical reaction three processes occur: activation, reaction of the activated product, and deactivation. These processes can be described quantum mechanically and they must *all* be taken into account. As an example the case of predissociation of diatomic molecules is considered. Here activation is by light, and after a lapse of time the molecule decomposes. It is shown that, under some circumstances which are discussed in detail, the wave function immediately after the excitation by light may be completely and correctly described as the wave function of a discrete state, which interacts with a continuum. Here the calculation of the rate of dissociation previously made by Wentzel applies, with some limitations which are discussed. Not all the simplifications which make the case of predissociation easy hold for decompositions of complicated molecules, but something is to be learned by comparing the two cases. The perturbations which give rise to the decompositions are of the same nature as those which occur in the case of predissociation, but they cannot be put into the same equation to give the rate of reaction. The reason for this is discussed, as are some of the questions involved in activation by collision.

INTRODUCTION

IN GENERAL the course of a unimolecular reaction seems to be as follows. A molecule is first excited, either by collision with other molecules as indicated by the best evidence in the case of thermal reactions,² or by radiation in the case of photochemical reactions. The excited or activated molecule may afterwards either break up, as in the case of a decomposition, or undergo a rearrangement or racemization. It is of course to be noted that the excited molecule may, on the contrary, be deactivated without reaction by subsequent collisions. The above description is typical of unimolecular reactions, and defines the class of reactions we shall consider. Note that a unimolecular reaction need not always be first order, as exemplified by numerous gaseous decompositions.²

Let us now attempt to describe the above in quantum mechanical terms. The first step, the activation, consists clearly in a quantum transition to a state of higher energy. The second step has been described as a quantum transition from one state to another state of the same energy.³ Strictly,

¹ National Research Fellow.

² For general discussion and references see Rice, *Comptes rendus Reunion International de Chimie Physique* (Paris, Oct., 1928), p. 298.

³ Langer, *Phys. Rev.* **34**, 92 (1929). See also Oppenheimer, *Phys. Rev.* **31**, 81 (1928); Rice, *Proc. Nat. Acad. Sci.* **15**, 459 (1929).

however, this description is not entirely accurate. The process of activation is truly a quantum transition, induced by external influences or perturbations. What happens after activation is in any event a very different sort of transition, but it may be treated as though it were quite similar under certain conditions, which we will investigate.

In a chemical reaction we are usually unable to isolate the activated molecule at all. We say that a reaction has occurred if we are able to distinguish the deactivated reaction products from the substances originally present; this will generally be the case if the reaction products cannot be brought into statistical equilibrium with the original system without going through the activated state in the reverse way. Thus we are interested in those cases in which the molecule in its activated state takes up configurations from which on subsequent deactivation it goes into a new product. Our actual process of calculation may be somewhat as follows. We subject the molecule to a perturbation starting at a definite time and acting for a certain length of time⁴ (the activating perturbation) and at a later time we again subject the molecule to a perturbation of finite endurance (the deactivating perturbation). We investigate the resulting wave function, expanding it in terms of the stationary eigenfunctions, and from the coefficients of the expansion may be derived the final distribution among the various stationary states in the known manner. We do not need to interpret the wave function for the intermediate activated state, but in practice it is necessary to follow its changes. Now we can follow its changes by means of the wave equation, theoretically, at any rate, and some consideration has been given this problem; but it must not be forgotten that the *whole* problem includes the finding of the initial condition, i.e., the state immediately following the activation; it also includes a consideration of the deactivation, but this will not be so important in the cases we shall consider.

Recently I have pointed out the similarity between the phenomenon of predissociation on the one hand, and that of unimolecular decomposition on the other.³ It will be interesting, therefore, to apply our process in some detail to the case of predissociation, though it will be found that the conditions which make the calculation for predissociation easy are not fulfilled for unimolecular reactions, and it will therefore be harder to carry over the results than I had at one time hoped; these results, however, will be a valuable aid in formulating the problem for the more difficult cases.

PREDISSOCIATION

Predissociation can occur when a molecule can be excited by absorption of radiation of a given frequency in two different ways, i.e., by two different

⁴ In photochemical reactions the time of illumination generally coincides with the time of reaction, and we can at any time measure the amount of reaction that has taken place, usually by means of a pressure measurement. We shall, however, in the following have occasion to consider the case, which may be rather artificial from the experimental point of view, in which the illumination is for a very short length of time, and the amount of reaction is determined if deactivation occurs at any subsequent time. This is similar to the case of activation by collision. The problem would probably take a somewhat different form if we considered collisions of molecules and light quanta.

electronic jumps, accompanied by the corresponding changes in vibrational and rotational quantum numbers.⁵ As in general one of the electron states will have a lower dissociation limit than the other, the continuum corresponding to the former will overlap discrete vibration-rotation levels of the other. Thus a molecule in one of these discrete states (a predissociated molecule) may be able to go by a radiationless transition to the overlapping continuum and dissociate. In this case activation is of course by radiation and we shall treat the case where the probability of transition directly from the initial state to the continuum is zero; i.e., the discrete state is a necessary intermediate. It is obvious that once the molecule is dissociated subsequent deactivation will in general leave it dissociated. We wish therefore to find the initial state after the absorption of light and then to follow the transition to the continuum.

In the above paragraph we have slipped into the old language in which we speak of transitions from one state to another of the same energy; it may then be questioned why we do not simply use the calculation already made by Wentzel,⁶ and it will be found that Wentzel's calculation is indeed applicable, at least under certain conditions, but the matter is not so simple as appears on the surface, and as far as I am aware has never been handled in a completely satisfactory manner. The reason for this will be apparent on going through the whole calculation.

In order to present this calculation we will need to proceed to a more definite formulation of our problem. We do this in the same manner as in previous work on predissociation.⁷ It will have been recognized by the reader that, if we speak of continuous and discrete eigenfunctions, these eigenfunctions will belong to an *approximate* wave equation which we write in the form

$$(H - E)\psi = 0 \quad (1)$$

where H is the usual Hamiltonian operator and E is the operator $(-h/2\pi i)\partial/\partial t$. This equation is built up in such a way that it has certain eigenfunctions ψ_a (not including the exponential time factor), with corresponding eigenvalues E_a , which correspond to discrete states, and others ψ_s , with eigenvalues E_s , which correspond to continuous states.⁸ Now let the exact equation be of the form

$$(H - E + V)\psi = 0 \quad (2)$$

⁵ There may be other cases in which predissociation can occur (see, e.g., Henri and Wolff, *J. Physique Radium* (6) **10**, 89 (1929)) but the one considered is typical.

⁶ Wentzel, *Phys. Zeits.* **29**, 333 (1928). Wentzel's calculation was made for the Auger effect, but can be applied unchanged to the case of predissociation. (See Kronig, *Zeits. f. Physik* **50**, 360 (1928).) Wentzel, *Zeits. f. Physik* **43**, 524 (1927) and Fues, *Zeits. f. Physik* **43**, 726 (1927) had previously made this calculation in another manner; but the meaning of this earlier work is harder to interpret and we will not consider it here.

⁷ Rice, *Phys. Rev.* **33**, 748 (1929).

⁸ We assume (see Ref. 7, pp. 749, 754) that the system is in a box, so that the continuous eigenvalues actually form a very close spaced discrete set.

where V is a perturbation function or operator. This equation will have eigenfunctions ψ_n' which have some of the properties of discrete states and some of the properties of continuous states; in other words, this equation takes into account the interaction of the discrete and continuous states. The eigenvalues E_n' are spaced like a continuous set, in a manner we have previously discussed.⁷ We express the perturbed eigenfunctions as linear functions of the unperturbed. If the discrete states are far enough apart⁹ we need consider only one of them at a time and can write

$$\psi_n' = S_{dn}\psi_d + \sum_s S_{sn}\psi_s. \quad (3)$$

Instead of a sharp line absorption when we shine light into the system there will be absorption over a finite width of energies, i.e., the line whose final state would have had the energy E_d will be broadened and the center will be at that energy E_n' for which S_{dn} has a maximum. We have assumed that the absorption is due to the discrete state, i.e., that $\int \psi_d P \psi_0 d\tau \neq 0$, where ψ_0 refers to the initial unexcited state and P is the electrical polarization, but that $\int \psi_s P \psi_0 d\tau = 0$. The intensity of absorption for a given perturbed state is proportional to $(\int \psi_n' P \psi_0 d\tau)^2$ and hence is proportional to S_{dn}^2 , ($d\tau$ is the volume element in configuration space and the integrals are taken over all allowable values of the coordinates.)

We are now ready to study the state of the system immediately following the absorption of light. Now we can control the nature of the light we shine in. Thus we might inquire what would happen if we were to shine in monochromatic light of just the right frequency, say, to excite a definite state ψ_n' . But if the light is to be strictly monochromatic we have to shine it in for an infinitely long time. So in this case there would be no sense in making any calculation regarding processes which would occur after activation, for activation will go on for an infinite length of time, after which the state of the excited molecule will be given by the stationary eigenfunction ψ_n' .

On the other hand, if we shine in light for an infinitely short time, then we may have any state excited. A case of particular interest arises if we shine in the light for so short a time that any energy over a considerable range in the neighborhood of one of the unperturbed discrete states ψ_d may be excited and that no appreciable decomposition takes place in that time, but for so long a time that only one ψ_d will be excited; we assume that this can be done. We shall see that it is a case to which the previously cited calculation of Wentzel's applies.

Let us suppose, then, that we have the molecule initially in the unexcited state ψ_0 , and shine in light of frequency equal to (or nearly equal to) $(E_0 - E_n)/h$ for some convenient length of time t . Let us follow the changes in the wave function describing the system. We expand it in the form¹⁰

$$\psi = a_0\psi_0 \exp(-2\pi i E_0 t/h) + \sum_n a_n \psi_n' \exp(-2\pi i E_n' t/h). \quad (4)$$

⁹ Ref. 7, pp. 751-2. Whenever we say that discrete states must be far apart, we mean that states which interact with each other must be far apart.

As we start with all atoms in the initial state, at $t=0$ all the a 's except a_0 are equal to zero, and a_0 may be taken as 1. Then after time t we have a_n (if its absolute value does not increase too much in time t) given by¹⁰

$$a_n = (2\pi\dot{P}_{n0}/ic\hbar) \int_0^t k(t) \exp [2\pi i(E_n' - E_0)t/\hbar] dt \quad (5)$$

where c is the velocity of light, $\dot{P}_{n0} = 2\pi i P_{n0}(E_n' - E_0)/\hbar$ where $P_{n0} = \int \psi_n' P \psi_0 d\tau$, and $k(t)$ is the magnitude of the vector potential of the light. $k(t)$ may be written as $k \sin [2\pi(E_d - E_0)t/\hbar]$, where k is a constant. Now we can put this in the integrand and integrate. If we do this it is easy to see that, if t is small compared to a period of the function $\exp [2\pi i(E_n' - E_0)t/\hbar]$ for all energies E_n' that are appreciably excited, the a_n of these states will be approximately in phase with each other, and proportional to P_{n0} .

It will be seen that the narrower the absorption line the easier it will be for the duration of illumination to be short enough so that all states which contribute appreciably to the absorption will be included without appreciable difference of phase, and long enough so that only states in the neighborhood of the one discrete state will be included.¹¹

We thus see that the initial state for the *decomposition*, which takes place after the absorption, is described by a wave function,

$$\psi = \sum_n a_n \psi_n' = \text{const} \times \sum_n P_{n0} \psi_n' \quad (6)$$

The exponential time factor, which, as we have seen is the same for all the terms at the beginning of the decomposition, is included in the constant. But we have previously seen that P_{n0} is proportional to S_{dn} , hence

$$\psi = \text{const} \times \sum_n S_{dn} \psi_n' \quad (7)$$

Now if we expand ψ_d in terms of the ψ_n' , which of course also form a complete orthogonal set, we get just the above expression (7), except for a constant factor. For the coefficient of any ψ_n' in the expression for ψ_d is equal to $\int \psi_d \psi_n' d\tau$, which is also equal to the coefficient S_{dn} of ψ_d when ψ_n' is expanded in terms of the unperturbed eigenfunctions.

Thus the initial condition for the decomposition is just that used by Wentzel, and hence his calculation is justified in the special case considered,

¹⁰ Dirac, Proc. Roy. Soc. **112A**, 673-5 (1926).

¹¹ If, however, the time of illumination is so short that other discrete states are excited the resulting situation may be reduced to the foregoing one by treating each discrete state separately. In the subsequent working out of the problem, however, one difference will result, as the coefficient a_s of a given continuous eigenfunction ψ_s will contain contributions from more than one discrete state. This will affect Eq. (12) below, as the square of a_s is not equal to the sum of the squares of the parts of which it is composed. However, for times t which are large enough so that the sum in Eq. (12) converges rapidly we may neglect the contribution to any given a_s from all the discrete states except one. Under these conditions, which are practically the conditions under which (12) is valid anyhow, we may treat each discrete state as if the decomposition from it were independent of all the others.

though with some further restrictions which we now discuss. We also justify certain assumptions not considered in detail by Wentzel.

Wentzel uses the method of Dirac.¹⁰ We set

$$\psi = a_d \psi_d \exp(-2\pi i E_d t/h) + \sum_s a_s \psi_s \exp(-2\pi i E_s t/h) \quad (8)$$

where the a 's are functions of t . As we have just seen, at $t=0$ (beginning of the decomposition from the predissociated state) we may put $a_d=1$ and all $a_s=0$, which furnishes the initial condition. Then

$$-(h/2\pi i) da_s/dt = a_d V_{sd} + \sum_{\substack{i=\text{all cont.} \\ \text{upper states}}} a_i V_{si} \quad (9)$$

where the matrix component

$$\begin{aligned} V_{mp} &= v_{mp} \exp[2\pi i(E_m - E_p)t/h] \\ \text{where} \quad v_{mp} &= \int \psi_m V \psi_p d\tau. \end{aligned} \quad (10)$$

If m and p represent two continuous states this may be considered negligible,¹² and consequently we write

$$-(h/2\pi i) da_s/dt = a_d V_{sd}. \quad (11)$$

To find the number of molecules in the state s at time t we integrate and evaluate $|a_s|$.² The total number of molecules in continuous states at time t

¹² In my previous article (Ref. 7, Appendix I) I have shown that v_{mp} (where m and p represent two different continuous states) will, at least under certain not unusual conditions, be very small compared to ϵ , the energy between two adjacent continuous states, provided the width of the line is small enough (see correction, end of this paper). If this is so the sum on the right (9) is negligible. For the value of a_i as found by Wentzel and used in obtaining (12) is

$$a_i = a_d v_{id} \frac{\exp[2\pi i(E_i - E_d)t/h] - 1}{E_d - E_i}$$

and we can use this as a first approximation in the sum, getting

$$\sum_i a_i V_{si} = a_d v_{sd} v_{si} \sum_i \frac{\exp[2\pi i(E_s - E_d)t/h] - \exp[2\pi i(E_s - E_i)t/h]}{E_d - E_i}$$

We have taken v_{id} outside as v_{sd} (see below and Ref. 13). The quantity under the summation sign has a maximum in absolute value when $E_d - E_i$ is equal to zero; it is then equal to $2\pi i t/h$. The quantity in the numerator is a periodic function; it has gone through a period when the energy E_i has passed through a range equal to h/t . The number of terms in this range is $h/\epsilon t$. Consequently the sum will be of the order of magnitude of $(2\pi i t/h) \times (h/\epsilon t) = 2\pi i/\epsilon$ and $\sum_i a_i V_{si} \sim 2\pi i a_d v_{sd} (v_{si}/\epsilon)$ and is consequently negligible.

If v_{mp} is not zero when $m=p$ Eq. (9) becomes $-(h/2\pi i) da_s/dt = a_d V_{sd} + a_s v_{ss}$. This is a case which very likely occurs, but it will be readily seen that $d|a_s|^2/dt$ is not altered at all, so that our subsequent calculations are unchanged.

is approximately (the approximation consisting in setting a_d constant in the integration)

$$\sum_s |a_s|^2 = |a_d|^2 \sum_s v_{sd}^2 \left| \frac{\exp [2\pi i(E_s - E_d)t/h] - 1}{E_d - E_s} \right|^2. \quad (12)$$

If a change of phase of a_d occurs during t Eq. (12) is changed only by having $E_d - E_s$ everywhere replaced by $E_d - E_s + \text{const.}$, which does not change the value of the sum if it can be replaced by an integral, as it usually can (see below): hence (12) is valid if $|a_d|^2$ does not change appreciably in time t . On account of the smallness of the matrix components of the perturbation for two continuous states, this will continue to give the increase in $\sum_s |a_s|^2$ for any small interval of time, provided the new value of $|a_d|^2$ is inserted, until $|a_d|^2$ becomes so small that the last term in (9) is no longer negligible. The increase in $\sum_s |a_s|^2$ is equal to the decrease in $|a_d|^2$, and this may be demonstrated directly by putting the expression for a_s found from integrating (11) into the proper expression for da_d/dt , integrating, and making the necessary calculation (using footnote 19, below).

The quantity under the summation sign in (12) has a maximum when $E_s - E_d \sim 0$. This maximum is sharp if t is not too small, and since the quantity v_{sd} is a slowly varying function¹³ of E_s we may under these conditions take it outside the summation sign. If t is sufficiently small or the box in which the system is enclosed is sufficiently large so that the quantity under the summation sign varies in an approximately continuous manner, we may replace this sum by an integral, finding for the fractional decrease per unit time, or the specific rate of dissociation, the expression (which it is to be noted does not involve the time, and hence gives rise to an exponential decrement)

$$\gamma = 4\pi^2 v_{sd}^2 / h\epsilon \quad (13)$$

ϵ being the energy difference between two adjacent continuous states.⁸ By a different normalization of the continuous states we can get rid of the ϵ , making the expression coincide with Wentzel's. From the expression previously derived for the width of the line,¹⁴ w , we see that

$$wT = h/2\pi \quad (14)$$

where $T = 1/\gamma$ is the average life of a molecule in a discrete state.

The assumptions which we have made are not entirely independent of each other, and it will be well to find the minimum conditions under which (13) can be taken as giving the proper value of the rate of dissociation. We note that the condition that (12) converges rapidly means that the function $\exp[2\pi i(E_s - E_d)t/h]$ should go through many periods as $E_s - E_d$ varies from zero to a value equal to the energy difference between the state d and the next discrete state. But this is just the length of time that light must

¹³ Ref. 7, p. 753.

¹⁴ Ref. 7, Eq. (34).

be shone in in order that only one discrete state should be excited. But the light must be shone in for such a *short* time that $\exp[2\pi i(E_n' - E_d)t/h]$ will go through only a small fraction of a period, provided the state of energy E_n' is appreciably excited. This means that, if Δt is this time,

$$w\Delta t \ll h/2\pi \quad (15)$$

Hence

$$\Delta t \ll T. \quad (16)$$

It seems that it should be safe to use (13) as an approximation, unless something very unusual occurs, even for $t < \Delta t$. So we see that very little decomposition will take place in the time of illumination, and also, therefore, in the time before the sum in (12) converges rapidly. We can formulate the important independent conditions necessary to make (13) valid (for practically the whole of the decomposition) as follows:

I. The time of illumination must be short compared to the life period of the molecule in its discrete state, and long enough so that only one discrete state is excited (though in view of reference 11 the latter is not so important).

II. The absorption must be small enough so that (5) holds.

III. The perturbation function v_{sd} must be so small that the broadened discrete states are still very narrow compared to the distance between the discrete states, and it may be readily verified that this is roughly equivalent to saying that the time of dissociation is large compared to the time of vibration of the atoms in the discrete states; also it is tacitly assumed that there is no interaction with other electronic states (and this is in general possible because of the wide spacing of electronic states, which is in turn connected with the extremely rapid motion of the electrons about the nuclei);¹⁵ in fact, there should be no other discrete state near.⁹

IV. The summation on the right hand side of Eq. (9) is negligible.

V. Absorption of light does not take place directly to the continuum.

VI. v_{sd} is a slowly varying function of E_s .

COMPARISON OF PREDISSOCIATION AND UNIMOLECULAR DECOMPOSITIONS

First, let us compare the perturbations responsible for predissociation and unimolecular decompositions. Formally they can both be treated in the same manner. The method is the one usually used in the treatment of molecules,¹⁶ and the perturbations which arise have been discussed by Slater.¹⁷ Take first the case of predissociation of a diatomic molecule.¹⁸ We consider first the distance r between the nuclei as fixed, and work out the wave equation

¹⁵ Born, "Vorlesungen über Atommechanik" (Springer, 1925), p. 114.

¹⁶ See, e.g., Condon, Proc. Nat. Acad. Sci. **13**, 462 (1927).

¹⁷ Slater, Proc. Nat. Acad. Sci. **13**, 423 (1927).

¹⁸ This has been discussed by Kronig, Ref. 6. Our formulation differs only slightly from his, but ours enables us to include all perturbations which may arise as examples of one general type.

for the rotation of the molecule and the motions of the electrons. This wave equation has certain eigenfunctions and eigenvalues, Θ_m and E_m say, which depend on r as a parameter. We now set up the wave equation in r (i.e., in which r is the independent variable) inserting for the potential energy one of the eigenvalues E_m , which as previously noted are functions of r . We thus get an *equation* in r for every *quantum state* found with r fixed. Each of these equations has a set of eigenfunctions R_{mk} which depend on the electronic and rotational quantum numbers denoted by m as well as on the vibrational quantum number k . We now try the product $\Theta_m R_{mk}$ in the *complete* wave equation. We will in general find that this is not a solution of the complete wave equation but satisfies some other equation, and the difference between them may be used as a perturbation to get the solutions for the former from those of the latter, as the $\Theta_m R_{mk}$ form a complete orthogonal set.¹⁹ Now we assume that the eigenvalues E_m which we get by holding r fixed form a discrete set, or, rather, we assume any continuum is so far out of the energy range we are interested in that we may neglect it. Then R_{mk} will correspond to either a discrete state or a continuum according to the relation of the total energy of the system to the curve $E_m(r)$. It will be generally conceded that the above unperturbed eigenvalues and eigenfunctions will give in a fairly correct manner the energy levels and dissociation limits of a diatomic molecule, and hence the corresponding perturbations will give correctly such things as the rate at which a molecule goes from a discrete state to a continuum.²⁰

In like manner, in the case of a complicated molecule, if we know the products immediately after decomposition, we may take as one coordinate the distance, r , between the two groups which separate. Holding this r first as a fixed parameter we calculate all electronic, rotational, and vibrational states, and if there is only one way in which the molecule can dissociate this will give discrete sets of eigenvalues. We can proceed in the same manner as before, finally getting perturbations of the type found by Slater. If, however, the eigenvalues which we use in the second step of the above process are a complicated function of r which has a maximum, as in the curves considered in the theory of radioactivity,²¹ a special complication arises, as the matrix components may change very rapidly with the energy. If this happened in the case of predissociation v_{sd} would not be a slowly changing function of E_s and we could not take it outside of the summation sign in evaluating (12).

¹⁹ This property is of course assumed throughout our development. The perturbed eigenfunctions must also form a complete orthogonal set. From these two facts we can conclude quite generally that the perturbation matrix is Hermitian (or, if we leave out the complex factor, as in the second part of (10), symmetrical). I am indebted to Dr. Morris Muskat for a proof of this fact. It renders certain details of my former paper unnecessary.

²⁰ Dr. Langer, in discussing this matter with me, has pointed out that such a conclusion always involves the assumption that convergence difficulties will not arise in calculating the perturbed eigenfunction. In this connection see foot note 16 of Ref. 7.

²¹ Gamow, *Zeits. f. Physik* **51**, 204 (1928); Gurney and Condon, *Phys. Rev.* **33**, 127 (1929). See also Langer, Ref. 3.

Let us consider the case of azomethane, where the first step in the decomposition is likely $\text{CH}_3\text{NNCH}_3 \rightarrow \text{CH}_3\text{NN} + \text{CH}_3$. Then we take for r the distance between the centers of gravity of the two groups on the right hand side of the equation. In so doing we neglect the resonance or interchange phenomenon as far as it concerns the nuclei in the two groups, which is probably justified. There is another difficulty. It is seen that it makes no difference which CH_3 group breaks off. There are thus effectively two ways in which the molecule can break up, and hence we may expect the appearance of a continuum even when r is held fixed, contrary to our assumptions. But a continuum occurs only when there is a rather large energy in the bond which breaks. Thus it is not often that we have to consider two continua at the same time, so it seems probable that to a first approximation our method is correct. Or, if we preferred, we could consider the *two* distances fixed at first, and our calculations would not be greatly altered.²² It thus seems that we have a fairly clear schematic picture of how the perturbations could be calculated theoretically; but it must not be supposed that even if these perturbations could actually be found that we could blindly put them into Eq. (13) and proceed to use it without further thought.

The difficulty lies chiefly in the failure of assumption III on p. 1458. In the case of a large molecule there is a complex series of changes in which energy passes from one place in the molecule to another. There is no reason to believe that there is not a large chance for decomposition to take place before such a cycle of changes is completed, or before the molecule comes back even approximately to its initial state. Although this interchange of energy involves vibrational motions probably entirely, the situation is somewhat similar to that which would occur in the case of predissociation if the electronic motions were slow. In that case assumption III would not be expected to hold, and we could not use deductions based on it.

It is of interest to note that assumption I is fulfilled, inasmuch as the time of activation, which extends through the duration of a collision, is in general short compared to the time for reaction to occur after a collision. It seems safe, therefore, at least in many cases²³ to conclude that at the collision the broadened discrete state is excited as a whole as if it were not broadened, just as in the case of predissociation the total absorption over the width of the line is equal to the total absorption which would occur if there were no interaction with a continuum. We can therefore calculate the rate of activation just as if no subsequent decomposition were going to take place. Gen-

²² This would be safe to do in case two CH_3 broke off simultaneously. See Ramsperger, J. Am. Chem. Soc. **51**, 2141 (1929).

²³ In the case of the decomposition of azomethane, which has been extensively studied (see, e.g., Rice and Ramsperger, J. Am. Chem. Soc. **50**, 617 (1928)) the conclusion seems quite safe, as the rate of reaction has only decreased by about 20% at a pressure of 1/10 atmosphere where the mean free path will be of the order of 10^{-5} cm. If a collision takes place in a distance of less than 10^{-7} cm, as we suppose to be the case, the time between collisions should be over 100 times the time of a collision, and since most of the molecules have not reacted in the time between collisions, it seems very probable that our conclusion will be valid.

erally this calculation is made by means of the principle of entire equilibrium or microscopic reversibility, in that we take the rate of activation to be equal to what the deactivation would be if the reaction did not occur.²⁴ This requires the calculation of the equilibrium number of activated molecules, which it is now seen must be made as though the discrete states were not broadened. It must be noted, however, that the conclusion that the broadened discrete state is excited as a whole is only certainly true if all the other assumptions are fulfilled as well as assumption I, for it depends upon the truth of (14). It also depends on a relation connecting the range of internal energies, ΔE , excited in a collision (which corresponds to the range of energies excited by light in the case of predissociation) and the time Δt of a collision:

$$\Delta E \Delta t \gtrsim h/2\pi. \quad (17)$$

If both (14) and (17) hold then $\Delta t \ll T$ requires $\Delta E \gg w$. A consideration of the collision problem for two complex molecules, taking into account both the translational and internal energies, indicates that (17) holds. But (14) does not hold in the present case as assumption III does not hold. So our conclusion that $\Delta E \gg w$, is not certainly true, but it is probably true. Now to further draw the conclusion that the broadened discrete state is excited as a whole we need to prove a formula equivalent to Eq. (7). This rests on Eq. (5) or assumption II. This assumption, which amounts to saying that the activating perturbation is small, does not hold in the collision case. Indeed, a collision is an exceedingly violent affair, and two molecules can interchange energy in various ways. The problem is thus complicated, and we have the difficulty that there will be many intermediate states before the final state of the molecule is reached after the collision. But we make the assumption that a continuous state in the molecule can never be excited directly from any discrete state by collision with another molecule, i.e., decomposition occurs *after* the collision. Then the chance that a molecule will at any time get into a certain excited perturbed state ψ_n' whose energy lies in the range ΔE will depend upon the coefficient S_{an} in the same way as in the case of predissociation.²⁵ The phase considerations become more complicated, but not very different in character from those we considered in the case of predissociation, and so no phase differences are to be expected. Thus, without laying claim to any great rigor, we may state that it seems very probable that the discrete state will be excited as a whole.

The equivalent of assumption V probably holds in the case of molecular decompositions, but, as mentioned above, the equivalent of assumption VI may not. It is hard to be sure about IV.

The above considerations make it appear unlikely that it will soon be possible to replace the statistical treatment² of the problem previously given by a strict theoretical treatment.

²⁴ Rice and Ramsperger, J. Am. Chem. Soc. **49**, 1619 (1927).

²⁵ Note that a relation similar to that described by Eq. (7) will still hold even if more than one discrete state is involved due to the failure of assumption III.

Correction to my paper: Perturbations in Molecules and the Theory of Predissociation and Diffuse Spectra, Phys. Rev. 33, 748 (1929).

There is an error in Appendix I, which invalidates the proof that $v_{c_1c_1}/\epsilon \sim 10^{-4}$. The distance of separation of two rotation states was written $h_j^2/4\pi^2Mr_0$ instead of $h_j^2/4\pi^2Mr_0^2$ and this was carried through. When the correction is made $v_{c_1c_1}/\epsilon$ turns out to be of the order of 1, and hence would appear not to be negligible. The Appendix still shows, however, that if the line is narrow enough $v_{c_1c_1}/\epsilon$ will be small, so our deductions hold for this case. The width of the line considered in Appendix I was actually rather large, and in many cases, at any rate, $v_{c_1c_1}/\epsilon$ may still be expected to be small. This is seen as follows. From Eq. (34) and the relations deduced in Appendix I between $v_{c_1d_1}$ and $v_{c_1c_1}$ we find $v_{c_1c_1}/\epsilon = (r_0W/2\pi r_1\epsilon)^{1/2}$. Now if we change r_1 we do not change the value of this expression. If r_1 becomes of the order of r_0 then ϵ will be of the order of the distance between two vibration levels. Hence if W is small compared to this distance $v_{c_1c_1}/\epsilon$ may be expected to be small. (When we allow r_1 to become small, we must do it in an idealized way, neglecting the effect of the actual potential energy curve at small r , as only thus will the expression under the radical remain unchanged.)