activations are discussed in terms of probabilities of energy transfer from electrons to normal molecules and of probabilities of further reaction between activated states and the mercury surface.

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ENERGY EXCHANGE IN UNIMOLECULAR GAS REACTIONS

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§1. Introduction

There is a large number of substances which decompose in the gas phase, and whose rate constants show a characteristic behavior in that they tend to approach a constant value as one goes to high pressures, but fall in value as one goes to low pressures.[1] According to the currently accepted theories, it is supposed that in these reactions the activated molecules receive their energy by collision with other molecules. As one goes to lower pressures the time between collisions becomes greater; when it becomes of the same order of magnitude as the average time necessary for an activated molecule to decompose, the falling off of the rate constant first becomes noticeable.[2]

Now it is found that it sometimes is possible to restore the rate constant to its high pressure value by the addition of an inert gas, which is able to exchange energy (without any chemical reaction taking place) with the molecules which are to decompose. Thus Hinshelwood and his co-workers have found that the rate constants for a number of ethers are increased by addition of a sufficient amount of hydrogen, the hydrogen being in most cases about as effective pressure for pressure as the reacting gas itself. They have also found that the rate constant is but little affected by the addition of helium, nitrogen, carbon dioxide and other gases composed of relatively heavy atoms;[2] also, strangely enough, in one or two cases, organic compounds have been reported ineffective.[3]

[1] As a matter of fact, in many cases, including those in which we shall be most interested here, this is a statement of a theoretical expectation rather than an experimental fact, since the limiting high pressure rate has not been reached experimentally.

[2] For a general discussion and references see Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., New York, 1932. It may be well to state explicitly that I assume the current explanations of the phenomena of unimolecular reactions, including the phenomena with inert gases present, although I am not certain but that further experimental work may show that some of the individual cases cited as illustrative of these principles really are more complex than they are now thought to be. In this connection note Rodebush and Copley, THIS JOURNAL, 54, 2560 (1932), and Vernon and Daniels, ibid., p. 2563.

[3] For example, Steacie, J. Phys. Chem., 36, 1562 (1932), reports that dimethyl and diethyl ether will not activate each other. These results have not been verified

As a start toward the development of an adequate theory of the exchange of energy in these gas reactions, we shall in this paper discuss the effects of hydrogen and helium.[4]   These will be the simplest cases to investigate, as they will involve only the exchange of rotational and translational energy; it seems probable that the vibrational energy of hydrogen will not enter into the problem appreciably.

Even this simplest case is in reality exceedingly complicated.   It will, therefore, be necessary to simplify the problem considerably.   So, in order to get a rough idea of how the process of energy exchange between the translational motion of the colliding particles and the vibrational motion of the decomposing molecule takes place, we shall consider the case of the collision of a simple particle with an oscillator whose equilibrium position is fixed in space (representing one of the oscillators in the reacting molecule—the particular one hit by the colliding particle).   We shall further assume that the oscillator is vibrating along some particular line in space, and that the particle is moving in the same line—thus we get a head-on collision.[5]   Crude though this model is, it will undoubtedly give us an indication of what actually does take place.

§2.   The Rotational Energy of the Colliding Molecule

When the colliding molecule is diatomic as in the case of hydrogen, the collision process is somewhat more complicated than in the case considered above on account of the possibility of exchange of rotational energy.   If the position of the colliding molecule were so fixed that its axis lay along the line of the collision, and if no exchange of vibrational energy takes place, then the collision should take place about as represented above.   But collisions will take place in which the colliding molecule is oriented in various ways.   Furthermore, the colliding molecule may hit the oscillator in such a way that the two atoms in the colliding molecule straddle the oscillator; or the collision may perhaps be rather a collision between one of the atoms in the molecule and the oscillator.   If the latter were the case, and if the colliding molecule were oriented across the line of the collision, the collision should be very much like the collision described before, but with the mass of the atom involved substituted for the mass of the whole colliding molecule.   The problem is thus reduced back to the situation originally considered of a particle colliding with an oscillator.

Of course, this discussion is based on much too crude a picture of a dumb-bell molecule; and, indeed, Eyring and Slater[6] have concluded that for ordinary collisions

by Kaşsel, THIS JOURNAL, **54**, 3949 (1932), however, to whom I am indebted for being allowed to see his results before publication.   Also, Hinshelwood and Askey, *Proc. Roy. Soc.* (London), **115A**, 215 (1927), have reported methane ineffective in the case of methyl ether, and in one or two instances Hinshelwood and his co-workers have reported the reaction products as slightly effective (propionic aldehyde) or even retarding (diethyl ether).

    [4] I have treated this problem in a rather hasty way in a previous article, *Chem. Rev.*, **10**, 125 (1932); there, however, I assumed that exchange of energy could only take place with the outside hydrogens of the organic molecule, an assumption which now seems to me to be too restrictive.

    [5] See Zener, *Phys. Rev.*, **37**, 556 (1931).

    [6] See Eyring, *Chem. Rev.*, **10**, 116 (1932); Eyring, THIS JOURNAL, **54**, 3191 (1932).

between two hydrogen molecules with a relative kinetic energy equal to the average at room temperature they act much like two spheres. It hardly seems possible at the present time to give a very satisfactory discussion of this question; these rough considerations will, however, provide the reason for making calculations, in the subsequent pages, in which the mass of the colliding particle is set equal to that of a hydrogen atom.

§3. The Transfer of Energy between a Colliding Particle and an Oscillator

The one-dimensional problem of a particle colliding with an oscillator, just outlined, has been treated by Zener,[5] by the following method. If the oscillator is in a certain energy state, it will exert a certain average force on the colliding particle which may be supposed for the moment to be held at a fixed distance from the point of equilibrium of the oscillator. This force depends on the distance of the particle, and one may thus construct a potential energy curve for the particle, there being a different potential energy curve for each state of the oscillator. Now the fact that the oscillator is actually in motion introduces a perturbation into the problem, which may be shown to result in an exchange of energy between the oscillator and the particle, and the probability of such an exchange may be calculated.

This may be formulated in the following manner. We let the distance of the oscillator from its center of equilibrium be x, and the distance of the colliding particle from the same point be r, the distance between the colliding particle and the oscillating particle being thus $r - x$; the eigenfunction which describes the state of the oscillator we call ϕ. If the colliding particle is far away, ϕ will very approximately satisfy the wave equation of a harmonic oscillator

$$\frac{h^2}{8\pi^2 m} \frac{d^2\phi}{dx^2} + (E - 2\pi^2\nu_0^2 m x^2)\phi = 0 \qquad (1)$$

where m is the mass of the oscillating particle, ν_0 its frequency, E its energy and h Planck's constant.

The effect of a collision of the colliding particle will be to change the oscillator from one state, say ϕ_n with energy E_n, to another, say $\phi_{n'}$, with energy $E_{n'}$, the difference of energy being taken up in the translational energy of the colliding particle. Suppose we represent the mutual potential energy of the colliding and the oscillating particles, which will be a function of $r - x$, by V. Then the average potential energy, when the colliding particle is fixed at a definite value of r and the oscillator is in a definite quantum state, n, will be a function of r given by

$$u_{nn} = \int_{-\infty}^{\infty} \phi_n^2 V \, dx \qquad (2)$$

The wave function of the colliding particle R_{nm} will, in zero approximation, obey the wave equation

$$\frac{h^2}{8\pi^2 M} \frac{d^2 R_{nm}}{dr^2} + (T_{nm} - u_{nn})R_{nm} = 0 \qquad (3)$$

where M is the mass of the particle and $T_{nm} = W_{nm} - E_n$ (W_{nm} being the total energy of the system). The wave function of the combined system will be, in zero approximation

$$\psi_{nm} = \phi_n R_{nm} \tag{4}$$

The normalization of the function R_{nm} which is one of a continuous series of eigenfunctions is accomplished in the following manner. We assume that r cannot become greater than a certain large value, r_∞. Then the continuum is changed into a close-spaced set of discrete states, the energy between two adjacent energy levels being

$$\epsilon_{nm} = 2\pi T_{nm}^{1/2}/r_\infty K \tag{5}$$

where $K^2 = 8\pi^2 M/h^2$. R_{nm} is then normalized so that

$$\int_0^{r_\infty} R_{nm}^2 dr = 1 \tag{6}$$

Now the wave equation for the whole system is

$$\frac{h^2}{8\pi^2 m} \frac{\partial^2 \psi}{\partial x^2} + \frac{h^2}{8\pi^2 M} \frac{\partial^2 \psi}{\partial r^2} + (W - 2\pi^2 \nu_0^2 m x^2 - V)\psi = 0 \tag{7}$$

When (4) is substituted into (7) it is found that the latter is not exactly satisfied. Treatment of the extra terms by the usual first order perturbation method shows that transitions are induced from the state nm to others, for example $n'm'$, with the same total energy. The transition probability is given by

$$\gamma_{nm,\, n'm'} = 4\pi^2 v_{nm,\, n'm'}^2/\epsilon_{nm}\epsilon_{n'm'} \tag{8}$$

where

$$v_{nm,\, n'm'} = \int_0^{r_\infty} R_{nm} R_{n'm'} u_{nn'} dr \tag{9}$$

where

$$u_{nn'} = \int_{-\infty}^{\infty} \phi_n \phi_{n'} V\, dx \tag{10}$$

$R_{n'm'}$ satisfies an equation like (3) but with $u_{n'n'}$ substituted for u_{nn} and $T_{n'm'} = E_n - E_{n'} + T_{nm}$ for T_{nm}.

§4.   Calculation of Transition Probabilities

The evaluation of $\gamma_{nm,\, n'm'}$ resolves itself into several parts. First we calculate u_{nn}, $u_{n'n'}$ and $u_{nn'}$. The first two of these enable us to get R_{nm} and $R_{n'm'}$. Then, finally, we can find $v_{nm,\, n'm'}$ and $\gamma_{nm,\, n'm'}$. All of these calculations require us to make approximations. In order to check up on these we shall try different methods of approximation, the results of which we can then compare.

The interaction, V, of the colliding and oscillating particle can be approximated by a function of the form

$$V = Ce^{-\alpha(r - x)} \tag{11}$$

C is a constant and α is a parameter which determines what we may call the "sharpness" of the collision.[5] The determination of these constants will be discussed in a later section.

With this expression for V, and remembering that the solutions of

equation 1 are the Hermite orthogonal functions, it is easy to arrive at expressions for u_{nn}, $u_{n'n'}$ and $u_{nn'}$. These expressions will all be of the form $e^{\alpha^2/4\beta - \alpha r}$ times a polynomial in $\alpha/\beta^{1/2}$ where

$$\beta = 4\pi^2 m\nu_0/h \tag{12}$$

But the insertion of a function of this form into equation 3 will not give an equation which can be solved for R_{nm}. It is necessary, therefore, to find some other type of approximation for u_{nn}. This is accomplished in the following way. We set

$$u_{nn} = A/(r - B)^2 + u_\infty \tag{13}$$

The constants A, B and u_∞ are then adjusted so that u_{nn}, du_{nn}/dr and d^2u_{nn}/dr^2 have the proper values (i. e., the values equal to those found by the use of equation 11 in evaluating u_{nn}) at that value of r, which we call r_0, at which $T_{nm} = u_{nn}$. The values of A, B and u_∞ are

$$A = 27T_{nm}/2\alpha^2 \tag{14}$$
$$B = r_0 - 3/\alpha \tag{15}$$
$$u_\infty = -T_{nm}/2 \tag{16}$$

This gives an approximate value of u_{nn} which will be good in the region of r which is most important in determining the value of the integral in equation 9. In particular, it will differ from the true u_{nn} in two respects. First, it has the wrong asymptotic value. Second, it becomes infinite when $r = r_0 - 3/\alpha$. These differences lie outside the important region of r, as noted.

Having thus set up an expression of u_{nn}, we write for $u_{n'n'}$ simply

$$u_{n'n'} = \rho u_{nn} \tag{17}$$

where ρ is a constant equal to the ratio $u_{n'n'}/u_{nn}$ obtained by setting (11) in (2) and the similar expression for $u_{n'n'}$. We have

$$A' = \rho A \qquad B' = B \qquad u'_\infty = \rho u_\infty \tag{18}$$

where A', B' and u'_∞ are the parameters in the expression for $u_{n'n'}$.

With these values of u_{nn} and $u_{n'n'}$ we can express R_{nm} and $R_{n'm'}$ in terms of Bessel functions[7]

$$R_{nm} = (\pi Kz/r_\infty)^{1/2} (3T_{nm}/2)^{1/4} J_\nu(K \sqrt{3T_{nm}/2}\, z) \tag{19}$$
$$R_{n'm'} = (\pi Kz/r_\infty)^{1/2} (T_{n'm'} - u'_\infty)^{1/4} J_\mu(K \sqrt{T_{n'm'} - u'_\infty}\, z) \tag{20}$$

where the J's are Bessel functions of orders and arguments indicated, $z = r - B$, and

$$\nu = (K^2A + 1/4)^{1/2} \tag{21}$$

and

$$\mu = (K^2A' + 1/4)^{1/2} \tag{22}$$

Now if we let σ be the ratio $u_{nn'}/u_{nn}$ obtained through the substitution of (11) in (2) and (10) we may write

$$v_{nm, n'm'} = \sigma \int_0^{r_\infty} R_{nm}R_{n'm'}\, u_{nn}dr \tag{23}$$

[7] Watson, "Bessel Functions," Cambridge University Press, 1922, p. 95.

We may substitute for R_{nm} and $R_{n'm'}$ from (19) and (20) and for u_{nn} from (13). The most convenient quantity to get is $v_{nm,\,n'm'}/(\epsilon_{nm}\epsilon_{n'm'})^{1/2}$ using (23) and (5). We set

$$
\begin{aligned}
a &= (\nu + \mu)/2 \\
b &= (\nu - \mu)/2 \\
c &= \nu + 1 \\
S &= 3T_{nm}/2(T_{n'm'} - u'_{\infty})
\end{aligned}
\qquad (24)
$$

We consider the case where $S < 1$. Then the result of the integration indicated in (23) is[8]

$$
v_{nm,\,n'm'}/(\epsilon_{nm}\epsilon_{n'm'})^{1/2} = \frac{\sigma K^2}{6^{1/2}} \left(\frac{T_{nm}}{T_{n'm'}}\right)^{1/4} S^{\nu/2 - 1/4} \times
$$

$$
\left[-\frac{S}{K^2}\frac{\Gamma(a+1)}{\Gamma(c)\,\Gamma(-b)}\,F(a+1,\,b+1,\,c,\,S) + \left(\frac{3}{2}\right)\frac{A}{2}\frac{\Gamma(a)}{\Gamma(c)\,\Gamma(1-b)}\,F(a,b,c,S)\right] \quad (25)
$$

In this expression the Γ's represent the usual gamma functions, with the arguments indicated, while the F's are hypergeometric functions.

It will be noted that the first term in the brackets arises from the second term in the expression for u_{nn} (equation 13), which is responsible for the fictitious asymptotic value of u_{nn}. If, therefore, this term should prove to be relatively large, we should hesitate to use equation 25. It is small, however, provided S is not too close to 1, which will be true in the cases we shall consider in this paper. If this is true the hypergeometric function is about equal to 1, and the absolute value of the ratio of the second term to the first becomes roughly $3AK^2/4Sab = 3/S(1 - \rho)$, by equations 24, 21, 22 and 18. In the least favorable cases we shall have to consider this ratio, as may be verified from the subsequent calculations, will be around 20. So the first term of (25) may be neglected. Further, it will never cause more than about 4% error to set $(3T_{nm}/2T_{n'm'})^{1/4}$ equal to $S^{1/4}$. Also, for the hypergeometric function, in the range of the parameters we shall need to use, it will be a good approximation to set[9] $(1 - aS/c)^{-b}$. Equation 25 thus becomes (using equation 14)

$$
v_{nm,\,n'm'}/(\epsilon_{nm}\epsilon_{n'm'})^{1/2} = 3.74\,\sigma\,\frac{K^2 T_{nm}}{\alpha^2}\,S^{\nu/2}\,\frac{\Gamma(a)}{\Gamma(c)\,\Gamma(1-b)}\,(1 - aS/c)^{-b} \qquad (26)
$$

As a check on (26) another approximation for u_{nn} may be used in equation 23, still using the values of R_{nm} and $R_{n'm'}$ (which I think are certainly as good as we can get) given by (19) and (20). For the new approximation we shall set

$$
u_{nn} = 27T_{nm}/\alpha^3 z^3 \qquad (27)
$$

[8] Ref. 7, p. 401.

[9] This may be verified readily by comparison of the series expansions of the hypergeometric function and the function which is substituted for it. In doing this it is necessary, of course, to have at hand the values of the various parameters involved. Sufficient data are presented in the subsequent calculations so that these parameters may be calculated if it is desired to verify this procedure.

It may be verified that this expression gives the same values for u_{nn} and du_{nn}/dr, and 4/3 the former value for d^2u_{nn}/dr^2 at $r = r_0$. This approximation gives (making the allowable approximation $(T_{n'm'} - u'_\infty)^{1/4}/T_{n'm'}^{1/4} = 1$)

$$v_{nm, n'm'}/(\epsilon_{nm}\epsilon_{n'm'})^{1/2} = 4.57\,\sigma\,\frac{K^3 T_{nm}^{3/2}}{\alpha^3}\,S^{\nu/2 - 1/2}\,\frac{\Gamma(a - 1/2)}{\Gamma(c)\,\Gamma(3/2 - b)}\,F(a - 1/2, b - 1/2, c, S)$$

$$(28)$$

The hypergeometric function may be set equal $[1 - (a - 1/2)S/c]^{-b + 1/2}$. As a matter of fact, I have set it equal to 1 in using this equation, as this is a sufficiently good approximation.

§5. Interaction of the Oscillator with the Rest of the Molecule[10]

We now attempt to take into account the fact that the oscillator actually struck by the colliding particle is but part of a molecule whose motion should rightly be described in terms of its normal coördinates. As long as the molecule is not too highly excited, its wave equation will be separable in the normal coördinates, the motion of each coördinate will be quantized as an harmonic oscillator and have its own frequency, and the normal coördinates will be linear functions of the natural coördinates which describe the actual positions of the atoms in the molecule. Suppose the number of coördinates which we have to consider (i. e., the equivalent number of coupled linear oscillators, provided each contributes approximately an equal amount to the motion of the natural coördinate which gives the position of the atom actually struck in the collision) is q. We consider now the probability that the normal oscillator connected with one[11] of the q normal coördinates changes its quantum state. Then it may be readily shown that, to a good approximation, the results of the previous section will remain valid, if, in calculating the ratios ρ and σ, we simply substitute $\alpha^2/q\beta$ for α^2/β. The physical significance of this is clear. β is a parameter the inverse square root of which gives the extension in space of the motion of the oscillating particle. But the particular oscillating particle which is hit in the collision must now share its energy, so to speak, with other oscillators, and it is the energy of all these oscillators which is transferred at the collision. There will be less vibration of the particular atom in the molecule which is hit by the colliding particle, due to the energy of any given normal vibration, than there would be if all that energy were located in the given particle. Therefore β must be correspondingly larger. In general ρ will be found to be nearer 1 than in the previous section because the motion of the particular particle in the molecule which is struck will

[10] The problem considered in section 5 has something in common with the problem of accommodation coefficients recently considered by Jackson, *Proc. Camb. Phil. Soc.*, **28**, 136 (1932), and Zener, *Phys. Rev.*, **40**, 178, 335 (1932) and, since the submission of this article, Jackson and Mott, *Proc. Roy. Soc.* (London), **137A**, 703 (1932).

[11] We remember, of course, that there are now different ways in which such transitions can occur, a factor taken into account afterward.

not differ as much after the transition; the effective potential energy curves u_{nn} and $u_{n'n'}$ of the colliding particle before and after the collision will therefore be nearer alike.[12]

The mathematics of the situation is as follows. We will use the symbols $\xi_1, \xi_2, \ldots \xi_q$ to designate the normal coördinates, and $x_1, x_2, \ldots x_q$ to designate the "natural" coördinates. One of the latter, say x_1, will be the quantity that we have previously designated as x; that is, it is the displacement of the oscillator actually hit by the colliding particle in the direction along which it is hit. Now we shall be interested in the behavior of the coördinate x_1 when one of the normal modes of vibration is excited. (We can then find its behavior when more than one are excited, by simple addition.) To get this information we shall need to inquire into the dynamics of the molecular motion, and for the moment we shall look at it from a classical point of view.

The ξ's will be linear functions of the x's and we may write

$$\xi_i = \Sigma_j a_{ij} x_j, \text{ and} \tag{29a}$$
$$x_j = \Sigma_i b_{ji} \xi_i \tag{29b}$$

where $a_{ij} = \partial \xi_i / \partial x_j$ and $b_{ji} = \partial x_j / \partial \xi_i$. Although the ratios of the various b_{ji} (with a given i) are determined by the dynamical situation, the absolute values are not. We shall, therefore, apply what we may term a normalizing condition, which will determine the absolute values. If only one ξ_i is excited then $x_j = b_{ji} \xi_i$ and $x_j^2 = b_{ji}^2 \xi_i^2$; we shall now demand that on the average x_j^2 goes through the same range as ξ_i^2, so that on the average b_{ji}^2 is 1. This means that

$$\Sigma_j b_{ji}^2 = q \tag{30}$$

where q is the number of values j can take.[13]

Now the kinetic energy for the given normal mode of vibration is $\mu_i \dot{\xi}_i^2 / 2$, where μ_i is the reduced mass for the mode of vibration. But since the x_j are ordinary Cartesian coördinates of the actual particles of the system, we must have, $\mu_i \dot{\xi}_i^2 / 2 = \Sigma_j m_j \dot{x}_j^2 / 2$, if only one normal mode of vibration is excited. Here the m_j are the masses of the various parts of the system. But since only the one mode of vibration is excited, we must have, by (29b), $\dot{x}_j = b_{ji} \dot{\xi}_i$ and, hence, $\mu_i \dot{\xi}_i^2 / 2 = \Sigma_j m_j b_{ji}^2 \dot{\xi}_i^2 / 2$ which enables us to define our reduced mass (in a rather unusual way) as

$$\mu_i = \Sigma_j m_j b_{ji}^2 = q \overline{m}_i \tag{31}$$

where $\overline{m}_i$ is a sort of average of the masses of the parts of the system.

The wave equation for a normal mode of vibration of frequency ν_0 will be like equation 1, except that ξ_i, say, will replace x and μ_i will replace m. If the eigenfunction is $\phi^i(\xi_i)$ then the eigenfunction for the complete system, including all normal vibrations, will be of the form $\Pi_i \phi^i(\xi_i)$.

In place of equation 2 we now have

$$u_{nn} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} [\Pi_i \phi_n^i(\xi_i)]^2 V d\xi_1 d\xi_2 \ldots d\xi_q \tag{32}$$

Using equation 11 (remembering that x_1 takes the place of x) and equation 29b we get, after a slight rearrangement

$$u_{nn} = C e^{-ar} \Pi_i \int_{-\infty}^{\infty} [\phi_n^i(\xi_i)]^2 e^{ab_{1i}\xi_i} d\xi_i \tag{33}$$

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[12] This becomes clear in the subsequent applications—see equations 39 and 41.

[13] q will be equal to $1/3$ the value of the quantity called n by Rice and Ramsperger, THIS JOURNAL, **49**, 1617 (1927).

and similarly for $u_{n'n'}$. If the states n and n' differ in only one $\phi^i(\xi_i)$ which we designate simply with i, then we may write instead of the ratio ρ of equations 17 and 18

$$\rho_i = \frac{u_{n'n'}}{u_{nn}} = \frac{\int_{-\infty}^{\infty} [\phi_{n'}^i(\xi_i)]^2 e^{\alpha b_{1i}\xi_i} d\xi_i}{\int_{-\infty}^{\infty} [\phi_n^i(\xi_i)]^2 e^{\alpha b_{1i}\xi_i} d\xi_i} \tag{34}$$

Similarly in place of the ratio σ may now be written

$$\sigma_i = \frac{\int_{-\infty}^{\infty} [\phi_n^i(\xi_i)][\phi_{n'}^i(\xi_i)] e^{\alpha b_{1i}\xi_i} d\xi_i}{\int_{-\infty}^{\infty} [\phi_n^i(\xi_i)]^2 e^{\alpha b_{1i}\xi_i} d\xi_i} \tag{35}$$

Now $\phi_n^i(\xi_i)$ will be the same function of ξ_i as the previously considered function ϕ_n is of x, except that β_i will be substituted for β, where

$$\beta_i = 4\pi^2\mu_i\nu_0/h \tag{36}$$

The original expressions for ρ and σ will be functions of α^2/β. (This follows from the statement just before equation 12.) From their relation to the new ρ_i and σ_i defined in equations 34 and 35 it may readily be seen that the latter will be functions of $\alpha^2 b_{1i}^2/\beta_i$. Now b_{1i}^2 will be of the order of 1, from equation 30, while β_i will be of the order βq by (31), (36) and (12). Thus we may say, roughly, that ρ_i and σ_i are the same functions of $\alpha^2/q\beta$ as ρ and σ are of α^2/β. We shall see in section 6 how our results are affected by making this change.

§6.   Results of the Calculation

The vibration frequencies of organic molecules have been discussed by Andrews.[14]   In our calculations we shall try assigning a number of values to ν_0, i. e., 500, 1000 and 1500 wave numbers (cm.$^{-1}$) which are reasonable frequencies corresponding to various types of vibration of the component atoms.

Andrews also has considered the force constants of the oscillators in organic molecules.   The force constant, k_i, for a particular normal mode of vibration, is given by the expression $k_i = 4\pi^2\nu_0^2\mu_i$, while if we consider only a single oscillator as in section 4 we have

$$k = 4\pi^2\nu_0^2 m \tag{37}$$

The constant which Andrews has attempted to evaluate is k.   We have made calculations in which we have assigned to this quantity the values 0.6×10^5, 1.2×10^5 and 5.0×10^5 dynes per cm., which, from Andrews' work, would appear to cover satisfactorily the range likely to occur in organic molecules.   Our procedure is to get β from the equation (derived from 12 and 37)

$$\beta = k/h\nu_0 \tag{38}$$

using the given values of k and ν_0.   If we wish to take into account the considerations of section 5 we multiply this value of β by q.

Next we consider the extent to which the vibrations of an activated molecule are likely to be excited;   we are particularly interested in the

[14] Andrews, *Phys. Rev.*, **36**, 544 (1930).

ethers, as these are the cases in which data on the effect of inert gases are available.   Hinshelwood and his co-workers have found their activation energies to be around 50,000 calories per mole,[2] and in general the number of normal modes of vibration which seems to be associated with the decomposition, in these cases, is around five.   Thus in the activated molecule each one of these normal modes of vibration is excited on the average by an amount equivalent to 10,000 calories per mole.   If the frequency is 1000 wave numbers, corresponding to about 2850 calories per mole, it will be seen that this means that it is in its third or fourth quantum state. As this would seem to be a good average value, we have made calculations in which we assume that the vibrator goes from its fourth to its third quantum state giving up the energy to the colliding particle (we choose to consider deactivation rather than activation, this being in general more convenient from a theoretical point of view); but we have also investigated the case in which the oscillator goes from its first to its 0th (lowest) quantum state.

We come now to the properties of the colliding particle.   Its initial kinetic energy T_{nm} we set equal to the average translational energy of one component of the motion of a particle in thermal equilibrium at a temperature like those at which the reactions occur, say 800 Å., i. e., about 800 calories per mole.

We assign to M the value, in atomic weight units, of 1, 2 or 4, according to whether we are investigating the exchange of rotational energy by hydrogen, of translational energy by hydrogen, or of translational energy by helium.   (It would, of course, be proper to take into account the motion of the organic molecule by using a reduced mass.   This would lessen the difference between hydrogen and helium slightly.)

Finally we come to the evaluation of the constant α, which gives the sharpness of collisions.   The question of the interaction between molecules has been discussed by Lennard-Jones,[15] who gives a formula for the force between two hydrogen molecules as a function of the distance between them.   It will almost certainly produce no appreciable error to use this same curve for evaluating the force between a colliding hydrogen molecule and the oscillator in the organic molecule, as the force between two atoms does not seem to depend much on how they are bound to other atoms. Even though the colliding particle exchanges energy with the carbon-carbon vibrations, the force must probably be transmitted through hydrogen atoms.   If now we set $\alpha = 5 \times 10^8$ cm.$^{-1}$, use this in equations 14 and 15, and calculate u_{nn} from equation 13, we get a function of r which coincides reasonably well with what we would get from Lennard-Jones, in the important range of r.   This is illustrated by Fig. 1, in which the curve is the potential energy function from Lennard-Jones, and the circles

[15] Fowler, "Statistical Mechanics," Cambridge University Press, 1929, Chapter X.

represent points calculated in the way described. In the case of helium we have no very good way to calculate α. Helium may likely make a sharper collision than hydrogen. If, on the other hand, we use Lennard–Jones' curve for the collision of two helium atoms, we will undoubtedly get too sharp a collision, *i. e.*, too large a value of α. A mean between the curve for two hydrogen molecules and that for two helium atoms will probably be about right, and indicates a value for α for the collision of helium with an organic molecule of about 0.5×10^8 higher than the corresponding value with hydrogen. We have carried out calculations for a series of different values of α, to show how this parameter affects the results.
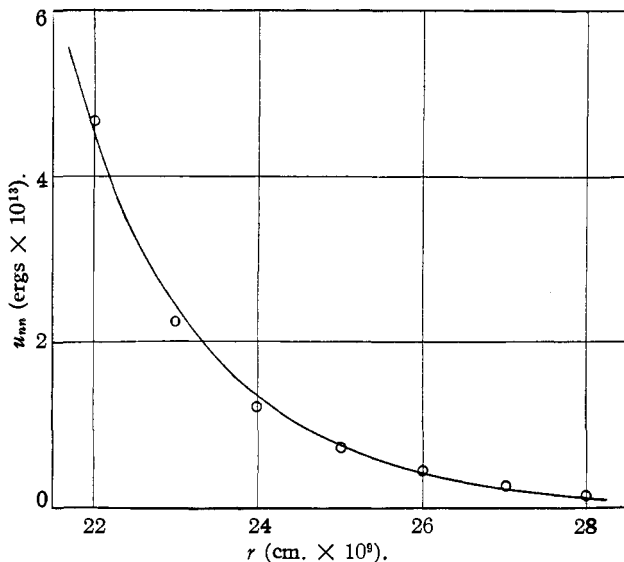

Fig. 1.

In Table I are given the results when we assume that ϕ_n, the eigenfunction of the initial state, is the eigenfunction of the first excited state of a harmonic oscillator, and $\phi_{n'}$ is the lowest state and use equation 26 for the calculation. It is here assumed that there is but a single oscillator, the results of section 5 not being taken into account. In this case it is easily shown that

$$\rho = (1 + \alpha^2/2\beta)^{-1} \tag{39}$$
$$\sigma = (\alpha^2/2\beta)^{1/2}(1 + \alpha^2/2\beta)^{-1} \tag{40}$$

In Table II we have used equation ˙28 instead of equation 26. It will be seen that the results correspond fairly well to the results in Table I for somewhat higher values of α. This is to be expected, inasmuch as the potential given by equation 27 goes up much more steeply for small values of r than that given by equation 13. It is certainly unlikely that any

TABLE I

VALUES OF $\gamma_{nm,\,n'm'}$ CALCULATED FROM EQUATION 26 (M IN ATOMIC WEIGHT UNITS, ν_0 IN CM.$^{-1}$, k IN DYNES PER CM., α IN CM.$^{-1}$)

M $\downarrow$	$\alpha \times 10^{-8}$ $\downarrow$ $k \times 10^{-5} \rightarrow$	$\nu_0 \rightarrow$ 500 0.6	500 1.2	500 5.0	1000 0.6	1000 1.2	1000 5.0	1500 0.6
1	7	0.40	0.31	0.10	0.13	0.14	0.070	0.053
1	6	.36	.25	.08	.11	.11	.047	.040
1	5	.27	.18	.060	.075	.070	.027	.024
1	4	.18	.11	.034	.037	.032	.012	.010
2	7	.31	.27	.10	.052	.072	.045	.012
2	6	.26	.21	.070	.035	.049	.027	.0067
2	5	.17	.13	.042	.019	.024	.011	.0033
2	4	.08	.063	.020	.0068	.0077	.0034	.0009
4	7	.15	.16	.074	.0077	.019	.018	.0006
4	6	.10	.11	.044	.0041	.009	.008	.0003
4	5	.051	.053	.021	.0017	.0034	.0025	.0001
4	4	.021	.019	.0070	.0004	.0007	.0004	.0000

TABLE II

VALUES OF $\gamma_{nm,\,n'm'}$ CALCULATED FROM EQUATION 28 (M IN ATOMIC WEIGHT UNITS, ν_0 IN CM.$^{-1}$, k IN DYNES PER CM., α IN CM.$^{-1}$)

M $\downarrow$	$\alpha \times 10^{-8}$ $\downarrow$ $k \times 10^{-5} \rightarrow$	$\nu_0 \rightarrow$ 500 0.6	500 1.2	500 5.0	1000 0.6	1000 1.2	1000 5.0	1500 0.6
1	6	0.42	0.29	0.087	0.25	0.21	0.080	0.16
1	4	.27	.17	.047	.10	.08	.027	.047
2	6	.39	.29	.100	.12	.13	.059	....
2	4	.17	.12	.036	.027	.025	.010	.0064
4	6	.22	.20	.080	.024	.037	.023	.0039
4	4	.060	.048	.017	.0026	.0034	.0017	.0002

general conclusions as to trends which would be drawn from the one set of calculations would not be drawn from the other also.   This gives us some confidence that these conclusions will be significant.

In Table III we have taken ϕ_n as the fourth excited state and $\phi_{n'}$ as the third, and we have used the considerations of section 5.   In this case it may be shown that, approximately (neglecting terms in the numerator and denominator containing higher powers of $\alpha^2 b_{1i}^2/\beta_i$)

$$\rho_i = \frac{1 + 1.50\,\alpha^2 b_{1i}^2/\beta_i}{1 + 2.00\,\alpha^2 b_{1i}^2/\beta_i} \sim \frac{1 + 1.50\,\alpha^2/q\beta}{1 + 2.00\,\alpha^2/q\beta} \tag{41}$$

and

$$\sigma_i = \frac{\alpha b_{1i}\,(1.41 + 1.06\,\alpha^2 b_{1i}^2/\beta_i)}{\beta_i^{1/2}\,(1.00 + 2.00\,\alpha^2 b_{1i}^2/\beta_i)} \sim \frac{\alpha\,(1.41 + 1.06\,\alpha^2/q\beta)}{q^{1/2}\beta^{1/2}(1.00 + 2.00\,\alpha^2/q\beta)} \tag{42}$$

where β is to be given the same value as in the case in which the considerations of section 5 were not taken into account.[16]   Now the transition

[16] The method of evaluating the matrices like u_{nn} and $u_{nn'}$ and, thus, ρ and σ is the following.   We can express the eigenfunction ϕ_n, as a function of the variable $\beta^{1/2}x = \xi$, as $\phi_n(\xi) = \pi^{-1/4} 2^{-n/2}(n!)^{-1/2} H_n(\xi)e^{-\xi^2/2}$, where $H_n(\xi)$ is a Hermite poly-

TABLE III

VALUES OF $\gamma_{nm,n'm'}$ CALCULATED FROM EQUATION 44 (M IN ATOMIC WEIGHT UNITS ν_0 IN CM.$^{-1}$, k IN DYNES PER CM., α IN CM.$^{-1}$)

M ↓	$\alpha \times 10^{-8}$ ↓	$\nu_0 \to$ 500 $k \times 10^{-5} \to$ 0.6	500 1.2	500 5.0	1000 0.6	1000 1.2	1000 5.0	1500 0.6
1	7	2.75	1.58	0.44	1.68	1.06	0.320	1.09
1	6	2.27	1.29	.34	1.27	0.76	.220	0.75
1	5	1.68	0.91	.24	0.78	.45	.125	.41
1	4	1.04	0.55	.138	.36	.20	.050	.155
2	7	2.81	1.63	.45	1.20	.75	.230	.601
2	6	2.09	1.19	.31	0.74	.44	.129	.325
2	5	1.31	0.71	.185	.35	.206	.057	.129
2	4	0.61	0.33	.082	.11	.061	.016	.031
4	7	2.16	1.25	.347	.53	.332	.102	.185
4	6	1.35	0.76	.203	.253	.152	.044	.072
4	5	0.66	.36	.093	.084	.049	.0135	.0188
4	4	.22	.118	.030	.016	.0086	.0023	.0022

VALUES OF $\gamma_{nm,n'm'}$ CALCULATED FROM EQUATION 44, BUT WITH T_{nm} = 2400 CALORIES, PER MOLE. ν_0 = 1000 CM.$^{-1}$

$\alpha \times 10^{-8}$ ↓	$k \times 10^{-5} \to$	$M = 1$ 0.6	5.0	$M = 2$ 0.6	5.0	$M = 4$ 0.6	5.0
6		6.70	1.16	4.75	0.83	2.09	0.36
4		2.38	0.35	0.99	.14	0.215	.032

probability calculated with the aid of these equations will be the probability that *one* of the normal modes of vibration will change its energy in the collision. Since there are actually q modes of vibration, the final $\gamma_{nm,\,n'm'}$ must be multiplied by q; or we can get an effective σ_i by multiplying it by $q^{1/2}$.

The actual value of q will be about 5; but we have already considered a case where q is equal to 1 and, involving lower quantum numbers, is much

nomial (see Sommerfeld, "Atombau and Spektrallinien," Ergänzungsbd, Braunschweig, 1929, pp. 19, 57). $\phi_n(\xi)$ differs from $\phi_n(x)$ in the normalizing factor, as $\phi_n(\xi)$ is normalized for integration with respect to ξ. Now, for example, consider $u_{nn'}$. We have

$$u_{nn'} = \pi^{-1/2} 2^{-\frac{n+n'}{2}} (n!n'!)^{-1/2} e^{-\alpha r} \int_{-\infty}^{\infty} H_n(\xi)H_{n'}(\xi) \, e^{-\xi^2} e^{\alpha x} \, d\xi \qquad (43)$$

By making the substitutions $\gamma = \alpha/2\beta^{1/2}$ and $\zeta = \xi - \gamma$ this takes the form

$$u_{nn'} = \pi^{-1/2} 2^{-\frac{n+n'}{2}} (n!n'!)^{-1/2} e^{-\alpha r} e^{\gamma^2} \int_{-\infty}^{\infty} H_n(\zeta + \gamma)H_{n'}(\zeta + \gamma) \, e^{-\zeta^2} \, d\zeta \qquad (43a)$$

Now $H_n(\zeta + \gamma)$ and $H_{n'}(\zeta + \gamma)$ may be expanded in terms of $H_n(\zeta)$ and $H_{n'}(\zeta)$, respectively, and their derivatives, by use of Taylor's theorem, and the derivatives of the Hermite polynomials may then be expressed in terms of Hermite polynomials of lower order (Courant and Hilbert, "Methoden der mathematischen Physik," Berlin, 1924, p. 76, equation 60) whence the integral reduces to a sum of integrals, all of which involving Hermite polynomials of different order vanish (Courant and Hilbert, equation 64), while the others are the standard normalization integrals (Courant and Hilbert, equation 65).

TABLE IV

σ_i, EFF., CALCULATED WITH THE AID OF EQUATION 42 (ν_0 IN CM.$^{-1}$, k IN DYNES PER CM., α IN CM.$^{-1}$)

$\alpha \times 10^{-8}$ $\downarrow$	$\nu_0 \rightarrow$ $k \times 10^{-5} \rightarrow$	500 0.6	500 1.2	500 5.0	1000 0.6	1000 1.2	1000 5.0	1500 0.6
7		1.073	0.815	0.430	1.356	1.073	0.592	1.521
6		0.954	.719	.370	1.230	0.954	.513	1.397
5		.825	.609	.310	1.082	.825	.434	1.245
4		.680	.496	.249	0.913	.680	.349	1.062

more sensitive to changes in ρ than the present one; furthermore, the differences between the results for given $h\nu_0$, given α, and given M, but differing k, are largely due to differences in σ. We shall therefore set $\rho_i = 1$ and write from equation 26

$$v_{nm,\,n'm'}/(\epsilon_{nm}\epsilon_{n'm'})^{1/2} = 3.74 \frac{\alpha}{\beta^{1/2}} \frac{1.41 + 1.06\ \alpha^2/5\beta}{1.00 + 2.00\ \alpha^2/5\beta} \frac{K^2 T_{nm}}{\alpha^2} \frac{S^{7/2}}{\nu} \tag{44}$$

This is the effective value of $v_{nm,\,n'm'}/(\epsilon_{nm}\epsilon_{n'm'})^{1/2}$ in which σ has been multiplied by $q^{1/2}$. Since ρ is set equal to 1 we have $\nu = \mu$, the gamma functions give the factor $1/\nu$ and the hypergeometric function becomes equal to 1. The results of the application of this formula have been given in Table III.[17]

It will be noticed that in some of these cases the transition probability has a value greater than 1. Such a result is of course impossible, and it means that the interaction between the oscillator and the colliding particle is so great that equation 8, which is based on the theory of small perturbations no longer holds. It may, in fact, well be that, even in cases where the transition probability comes out small, the perturbations are too large to apply the theory of small perturbations. For I have shown in the discussion of a similar problem that in the "case of poor resonance" such a thing may occur.[18] Now poor resonance means that there is a considerable exchange of translational to internal (which in the present case would be vibrational) energy, or *vice versa*, and this occurs in the cases considered in this paper. However, a method of treating the case of poor resonance when the perturbations are large has been developed.[19] This will now be applied and the results may then be compared with those we have already obtained. The latter have been presented in some detail because I believe that the relative values may have some significance; also, I think they may probably be used with slight modification in the case where the colliding particle may also have vibrational energy which it can exchange, a case which I hope may be the subject of future considerations.

[17] Because it may possibly be questioned whether one ought to set T_{nm} equal to 1/2 the Boltzmann constant times the absolute temperature rather than 3/2 this product, a few calculations are included in which T_{nm} is given the larger value.

[18] Rice, *Phys. Rev.*, **38**, 1951 (1931).

[19] Rice, *ibid.*, **38**, 1953 (1931); London, *Z. Physik*, **74**, 143 (1932).

§7. Modification for Large Interactions

In this calculation we consider two solutions of our equation 1, ϕ_n and $\phi_{n'}$ as before, but we first apply the perturbation V holding r fixed. Thus for the perturbed equation we have

$$\frac{h^2}{8\pi^2 m}\frac{d^2\phi}{dx^2} + (E - V - 2\pi^2 \nu_0^2 m x^2)\,\phi = 0 \tag{45}$$

in which r may appear as a parameter, but x is the only variable. We assume that ϕ_n and $\phi_{n'}$ are the *only* solutions of equation 1 that need to be considered. This is not true, but is necessary for purposes of simplification. Application of perturbation theory then shows that there are two solutions of (45) which we shall call χ_1 and χ_2 and which are given by[20]

$$\chi_1 = \phi_n \cos \omega + \phi_{n'} \sin \omega \tag{46}$$
$$\chi_2 = -\phi_n \sin \omega + \phi_{n'} \cos \omega$$

where

$$\omega = \frac{1}{2}\arctan\frac{2u_{nn'}}{E_n - E_{n'} + u_{nn} - u_{n'n'}} \tag{47}$$

The energies which go with these solutions are, respectively

$$U_1 = \frac{1}{2}\left\{ E_n + u_{nn} + E_{n'} + u_{n'n'} + [(E_n + u_{nn} - E_{n'} - u_{n'n'})^2 + 4u_{nn'}^2]^{1/2} \right\}$$

$$U_2 = \frac{1}{2}\left\{ E_n + u_{nn} + E_{n'} + u_{n'n'} - [(E_n + u_{nn} - E_{n'} - u_{n'n'})^2 + 4u_{nn'}^2]^{1/2} \right\} \tag{48}$$

We can now set up equations of the following form to give the translational motion of the colliding particle under the forces due to these potential energy fields

$$\frac{h^2}{8\pi^2 M}\frac{d^2 G_{kl_k}}{dr^2} + (W_{kl_k} - U_k)\,G_{kl_k} = 0 \tag{49}$$

where k takes the value 1 or 2, and l_k is the quantum number which then determines W_{kl_k}, the total energy. The eigenfunction giving the state of the whole system will be $\chi_k G_{kl_k}$. If such a wave function is substituted in the exact wave equation (7), however, it will be found not to satisfy it exactly. Treatment of the perturbation problem shows that if we start with the function χ_1 the probability per collision of going over to χ_2 (or *vice versa*) is given by

$$\gamma_{12} = 4\pi^2 p_{12}/\epsilon_1 \epsilon_2 \tag{50}$$

where p_{12} is the matrix component of the perturbation energy. If we simplify the subscript notation, calling the first (complete but unperturbed) eigenfunction $\chi_1 G_1$ and the second $\chi_2 G_2$ then

$$p_{12} = -K^{-2}\int_0^{r\infty} dr \int_{-\infty}^{\infty} dx \chi_1 G_1 [G_2(\partial^2 \chi_2/\partial r^2) + 2(\partial G_2/\partial r)(\partial \chi_2/\partial r)] \tag{51}$$

Substituting for χ_1 and χ_2 from (46) and (47), performing the differentiations and the integration with respect to x (taking into account the orthogonality of ϕ_n and $\phi_{n'}$ and the fact that they are normalized, and

[20] London, Ref. 19.

using some simple trigonometric identities) and integrating with respect to r by parts twice,[21] this can be written

$$p_{12} = K^{-2} \int_0^{r_\infty} \omega [G_2(d^2G_1/dr^2) - G_1(d^2G_2/dr^2)] dr$$

Using (49) this reduces to[22]

$$p_{12} = - \int_0^{r_\infty} \omega(W_1 - U_1 - W_2 + U_2) G_1 G_2 dr \tag{52}$$

Now it will be seen from equation 48 that since $u_{nn'}$ increases as r decreases U_2 may eventually reach a maximum. This would mean that though at first there is a repulsive force between the oscillator and the colliding particle, it becomes, if we go to small enough values of r, attractive. Such a result is, from a physical viewpoint, ridiculous. It apparently occurs because we have only taken into account the two states ϕ_n and $\phi_{n'}$, whereas in reality all states of the harmonic oscillator must be considered. When the perturbation becomes large, as at small values of r, a number of them will be of importance. However, with this method it will be very difficult to handle more than two states at a time. In this situation it seems best to make an attempt at an approximation by neglecting $u_{nn'}$ in equation 48, setting[23]

$$\begin{aligned} U_1 &= E_n + u_{nn} \quad \text{and} \\ U_2 &= E_{n'} + u_{n'n'} \end{aligned} \tag{53}$$

Furthermore, we have seen that when all the necessary considerations are taken into account it is a good approximation to set $\rho = 1$, that is, $u_{nn} = u_{n'n'}$. Thus (52) becomes, if we let $T_1 = W_1 - E_n$ and $T_2 = W_2 - E_{n'}$

$$p_{12} = -(T_1 - T_2) \int_0^{r_\infty} \omega G_1 G_2 dr \tag{54}$$

where G_1 and G_2 obey (49) with the values of U from (53) inserted.

This gives us the transition probability per collision from χ_1 to χ_2, but since at large distances χ_1 becomes equal to ϕ_n and χ_2 to $\phi_{n'}$ this will be the transition probability we desire. It is not pretended that this method gives better than a rough approximation, but it seems to me that there is no question that even this approximation will throw valuable light on the process of transfer of energy between molecules.

There is no way to evaluate (54) except by numerical methods. G_k (where $k = 1$ or 2) may be approximated by the Wentzel–Kramers–Brillouin approximation method,[24] which gives the following results. We set $r = r_k$ for the point where $W_k = U_k$ (that is $T_k = u_k$ if $u_k = u_{nn}$

[21] The integrated parts vanish at the limits.

[22] This is essentially equivalent to the equation for B_l on p. 165 of London's article. As it was not necessary for the purposes I had in mind at the time, I did not write out the expression 46 explicitly, and so did not get p_{12} into the form (52).

[23] The small disturbance due to the finite value of p_{11} and p_{22} is also neglected.

[24] See Kramers, Z. Physik, **39**, 828 (1926).

or $u_{n'n'}$ according as k is 1 or 2) and we assume the G's normalized in the same way as the R's, according to equation 6, and we take r_∞ to be very large; we may then write

$$G_k = 2^{1/2} r_\infty{}^{-1/2} T_k{}^{1/4} (T_k - u_k)^{-1/4} \cos \left\{ K \int_{r_k}^{r} (T_k - u_k)^{1/2} dr - \pi/4 \right\} \quad (55)$$

if $r \gg r_k$, and

$$G_k = 2^{-1/2} r_\infty{}^{-1/2} T_k{}^{1/4} (u_k - T_k)^{-1/4} \exp \left\{ -K \int_{r}^{r_k} (u_k - T_k)^{1/2} dr \right\} \quad (56)$$

if $r \ll r_k$. If r is in the neighborhood of r_k we may write

$$G_k = 2^{-1/2} r_\infty{}^{-1/2} \pi^{-1/2} K^{1/2} T_k{}^{1/4} \left\{ 3^{-1/6} \Gamma \left(\frac{1}{3} \right) (K^2 u_k')^{-1/6} + \right.$$
$$\left. 3^{1/6} \Gamma \left(\frac{2}{3} \right) (K^2 u_k)^{1/6} (r - r_k) \right\} \quad (57)$$
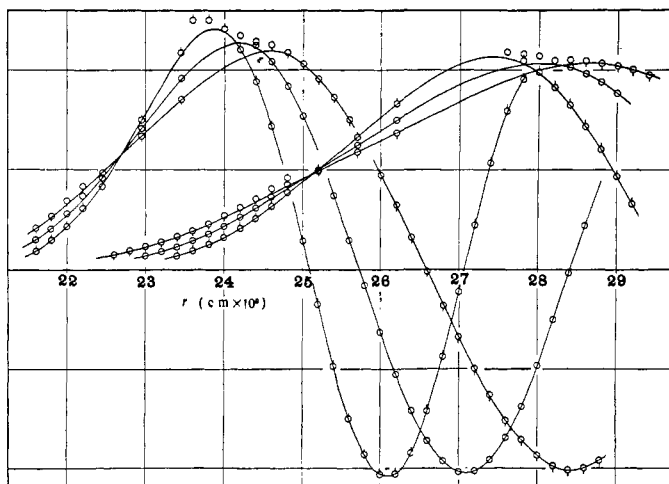
where $u_k' = -du_k/dr$.

Fig. 2.—Evaluation of G_k: $\varnothing$, $M = 1$; $\bigcirc$, $M = 2$; $\diamondsuit$, $M = 4$.

It is now necessary to evaluate G_k numerically. This we have done, using equations 53 (and $\rho = 1$) for determining U_k (U_1 or U_2). u_{nn} as a function of r we have taken directly from Lennard-Jones' expression for the force between two hydrogen molecules as a function of the distance between them. Since the equations 55, 56 and 57 do not cover the whole range of r it is necessary to interpolate between the various regions graphically. The method by which this has been done is shown in Fig. 2, in which portions of all the various G_k curves used in the subsequent calculation are exhibited. The three points near the first point of inflection of each curve ($r = r_k$) are, in each case, calculated from equation 57; the other points are calculated from either 55 or 56. The actual curves which have been used are shown. Values from these curves have been sub-

stituted into equation 54, ω has been calculated from (47) and p_{12} found by numerical integration. I have assumed that the value of $u_{nn'}$ to be used in (47) is obtained from u_{nn} by multiplication with the proper *effective* value of σ_i, as listed in Table IV. Calculations have been made for σ_i effective, equal to 0.5 and to 1.0.

On account of the labor involved in this process the calculations have been made for only a few cases. Throughout we have used the same curve for u_{nn} and have taken $T_1 = 0.5 \times 10^{-13}$ ergs (723 calories per mole) and $T_2 = 2.5 \times 10^{-13}$ ergs. The difference, $T_2 - T_1 = h\nu_0$, corresponds to an oscillator frequency of 1018 cm.$^{-1}$. The results of the calculations (γ_{12}) are given in Table V.

TABLE V
VALUES OF γ_{12} CALCULATED BY THE METHOD OF SECTION 7

$\sigma_{i,\,eff.}$	$M \rightarrow$	1	2	4
0.5		0.14	0.058	0.011
1.0		.32	.096	.007

Comparison with the values of Table III for $h\nu_0 = 1000$ cm.$^{-1}$ and $\alpha = 5 \times 10^8$ cm.$^{-1}$ indicates that the correction for large perturbations is scarcely necessary when $\sigma_{i,\,eff.} = 0.5$, but is of some importance when it is around 1.

Some information about how γ_{12} varies with the sharpness of collision may be found without further calculation by the following means. If we suppose that u_k has approximately the form $C_k e^{-\alpha r}$ we may make the substitution $y = \alpha r$ and write equation 49 in the form

$$\frac{h^2 \alpha^2}{8\pi^2 M} \frac{d^2 G_k}{dy^2} + (T_k - C_k e^{-y})G_k = 0$$

whence it is seen that, for given T_k and C_k, G_k will depend on α and M only in the combination α^2/M. Changing C_k is equivalent only to changing the zero point for y, which can make but very slight difference in the eigenfunction G_k, except to shift it along correspondingly. So if we have two eigenfunctions, G_1 and G_2, so long as the ratio C_1/C_2 remains fixed (for instance if $\rho = 1$) the product $G_1 G_2$ depends on α and M only in the combination α^2/M. If the same substitution, $y = \alpha r$, is made in (54), then it is readily seen, from (54), (50) and the fact that ϵ_1 and ϵ_2 are inversely proportional to $M^{1/2}$, that γ_{12} depends on α and M only in the combination α^2/M, except in so far as σ changes. Since Table V tells something as to how γ_{12} changes with σ, and with M when σ is fixed, one may estimate, with its aid and that of Table IV how γ_{12} will change when α changes and M remains fixed.

§8.   Discussion

The experimental facts, as far as they concern the effects of hydrogen and helium as activating and deactivating agents, are easily summarized.

Experiments have been made with hydrogen in the decompositions of dimethyl ether, diethyl ether, methyl ethyl ether, methyl propyl ether and propionic aldehyde. In all these cases, except methyl ethyl ether the hydrogen is about as effective pressure for pressure, in causing activation or deactivation as the organic molecule itself. In the case of methyl ethyl ether it apparently has somewhat less, but at least at the lower partial pressures of ether, a marked effect; at the higher partial pressures, it seems to retard slightly the rate in this case, but what this may mean is not clear.

In the case of dimethyl ether and diethyl ether, helium is said to be ineffective as an activator or deactivator. From the experiments[25] I should estimate that it is not more than about $1/15$ to $1/20$ as effective, pressure for pressure, as hydrogen. This estimate, however, is based on only one experiment in the case of dimethyl ether and two in the case of diethyl ether.

It has been customary in work on the kinetics of unimolecular reactions to assume that deactivation takes place at every collision of an activated molecule with an inactivated one of the same species. It was recognized, of course, that this could be only an approximation, and it was evident that the rate constants of the ethers fall off at a higher pressure than is to be expected for molecules of their complexity if we make the assumption of deactivation at every collision. However, it has been pointed out that this may be due to an impedance of energy transfer inside the molecule[26] or an ineffectiveness of certain of the vibrations of the molecule as far as the particular reaction is concerned;[27] so it is not necessarily to be ascribed to a failure of the assumption that deactivation takes place at every collision. The present results would seem to indicate that the assumption of deactivation at every collision is quite a reasonable one, as far as order of magnitude is concerned. For it seems to be definitely indicated that hydrogen will deactivate at a substantial fraction, say $1/10$ to $1/20$, of the collisions it makes; so the organic molecules, which are as effective, pressure for pressure, but which, on account of their slower average velocity, make only one-third to one-fourth as many collisions, will, within such a factor as is relatively unimportant in chemical kinetic considerations, deactivate at every collision with an activated molecule. (This is based on Table V.)

It should, perhaps, be remarked that removal of one quantum of energy (about 2850 calories per mole) from an oscillator of frequency around 1000 cm.$^{-1}$ is adequate to deactivate effectively an activated molecule. That is, it brings an average activated molecule into an energy range where the molecules are essentially maintained at their Maxwell–Boltz-

[25] Hinshelwood, *Proc. Roy. Soc.* (London), **114A**, 94 (1927); Hinshelwood and Askey, *ibid.*, **115A**, 223 (1927).

[26] Rice and Ramsperger, THIS JOURNAL, **50**, 619 (1928).

[27] Rice, "Réunion Internationale de Chimie Physique." Paris, 1928, p. 305.

mann quota.   Since similar discussions have been given before,[28] no detailed explanation will be given here, but the truth of the statement for practically any pressure is easily seen, if one accepts the theory of unimolecular reactions developed by Rice and Ramsperger, from their curves[29] giving the relative amount of reaction due to molecules of various energies.

And since the above results indicate that the supposition that only a limited number of the various modes of vibration are concerned with the reaction in the case of the ether decomposition is probably correct, it seems entirely reasonable to suppose that these particular vibrations have frequencies around 1000 cm.$^{-1}$, which is about that of a carbon–carbon or carbon–oxygen vibration when the vibration takes place in the line joining the two atoms.[30]

On this basis it would appear that the results of section 7 are fairly satisfactory in that they give a marked difference between hydrogen ($M = 2$) and helium ($M = 4$), even though it is not quite as large as the observed difference.   On closer examination, however, several doubtful points come to light.

In the first place the small values of γ_{12} for $M = 4$ in Table V are due to extensive cancellation of positive and negative parts in the integral for p_{12}. For example, in the case $M = 4$, $\sigma = 0.5$ the integral p_{12} is composed of three principal positive portions, equal to 3.5 p_{12}, 1.5 p_{12} and 0.05 p_{12}, respectively, from which are subtracted two principal negative portions equal to 4.0 p_{12} and 0.04 p_{12}, respectively.   The value of p_{12} will therefore be very sensitive to slight changes in the various quantities involved; thus if the curves for U_1 and U_2 as functions of r are shifted slightly with respect to one another, large changes in p_{12} will occur.   It is true that if these curves are shifted slightly apart (which is probably the right direction) p_{12} and hence γ_{12} will be decreased, but on the whole it will be easier to cause increases in p_{12} than decreases.   However, the important point is that when we have $M = 4$ we are already in the region of extensive cancellation of positive and negative portions of the integral, which is what is necessary to make it small.

A more unsatisfactory feature is our inability to make a fair comparison between the α for hydrogen and that for helium, and an estimate of the effect of changes in rotational energy in the case of hydrogen.   These two points are, of course, intimately associated, as both the value of α and the

[28] Rice and Ramsperger, THIS JOURNAL, **49**, 1625 (1927); Rice, "Réunion Internationale de Chimie Physique," Paris, 1928, p. 316.

[29] Rice and Ramsperger, THIS JOURNAL, **49**, 1625 (1927).

[30] It is not to be supposed. of course, that these are necessarily the only sorts of motion involved.   For example, the transverse hydrogen vibrations have a slightly higher frequency and may be of some importance.   In fact, in the case of dimethyl ether one cannot make up enough vibrations involving only the carbon–oxygen longitudinal motion.

possibility of exchange of rotational energy in the case of hydrogen are connected with the electron distribution in the hydrogen molecule. Although a direct collision of a helium atom would undoubtedly be sharper than one of a hydrogen molecule, it is by no means certain that this is true in the present case where transfer of energy from the carbon–carbon vibrations are concerned. For it is quite possible that the smaller size of the helium atom would enable it to get down into the interstices between the hydrogen atoms in the organic molecule, and so, in a certain number of its collisions, find it was bouncing off a softer cushion. In any event, it may well be that the possibility of a hydrogen molecule changing its rotational energy would make up for any smaller ability to exchange energy due to the blow being softer than in the case of helium.

But by far the most disconcerting factor, if one is interested in using the above results to explain the difference between hydrogen and helium, is a possibility that up to this point has been entirely neglected. This is the chance that transitions will occur in which two of the normal oscillators change their quantum states, one gaining, the other losing, energy. Since it is not possible for a given molecule to have around five oscillators of just the same frequency, it is quite possible that such a double jump would result in quite an appreciable transfer of energy to the colliding particle, though the amount of energy transferred would of course be much smaller than when only one oscillator changed its quantum number. A smaller exchange of energy is naturally less effective in producing deactivation, but on the other hand it will be found to take place with a greater probability, in spite of the fact that two oscillators are involved, and since for these transfers there is little difference between hydrogen and helium, the difference previously found will be to a large extent, masked.

An estimate of the probability of a transition involving a double jump may be made without too much calculation, using the method of section 7, if u_k is given approximately by $C_k e^{-\alpha r}$. If we write equation 49 in the form

$$\frac{h^2}{8\pi^2 M T_k}\frac{d^2 G_k}{dr^2} + (1 - C_k e^{-\alpha r} - \log T_k)\, G_k = 0$$

it is seen that a change of T_k has approximately the same effect on G_k as a change in M, with a shift in the abscissas. And a new value of σ_i, eff., is easily calculated by a slight extension of the methods previously used. Table VI gives some values of σ_i, eff., for ν_0 equal to 1000 cm.$^{-1}$ (this being assumed to be average frequency of the oscillators participating). These values are obtained from the values of σ_i by multiplying by $10^{1/2}$ instead of $5^{1/2}$, since 10 is the number of different pairs of 5 oscillators which is possible. (It is quite probable, of course, that not all the pairs would be effective, as with some pairs the available difference of energy would be too small to be at all effective in deactivation.) I have made a calculation of γ_{12}, taking $M = 4$, and $T_2 = 1.25 \times 10^{-13}$ ergs, as G_2 can then be obtained, as noted above, from the curves formerly used for $M = 2$ and $T_2 = 2.5 \times 10^{-13}$. This makes $T_2 - T_1 = 0.75 \times 10^{-13}$ ergs, instead of 2.0×10^{-13}. For σ_i, eff., $= 0.187$ and 0.375, respectively (values used because then ω does not need to be recalculated), I have obtained $\gamma_{12} = 0.077$ and

0.24, respectively. Values of γ_{12} for $M = 2$ will not be greatly different when the ratio of T_2/T_1 is so small. It is thus apparent that even though removal of 0.75×10^{-13} ergs is not as effective in deactivating as removal of 2.0×10^{-13} ergs, still the difference between hydrogen and helium will be pretty well swamped if these double jumps can occur.

TABLE VI

σ_i, EFF., FOR DOUBLE JUMPS FOR $\nu_0 = 1000$ CM.$^{-1}$ (k IN DYNES PER CM., α IN CM.$^{-1}$)

$\alpha \times 10^{-8}$ ↓	$k \times 10^{-5} \rightarrow$	0.6	1.2	5.0
7		1.377	0.844	0.250
6		1.119	.661	.188
5		0.865	.491	.133
4		.602	.331	.086

The alternative possibility is that the various normal modes of vibration are not as closely related as we have assumed, and that if the colliding molecule strikes the organic molecule in a certain way it interacts essentially only with a single oscillator, even though this be a normal oscillator.

On account of the points which have just been discussed, I do not feel that it is justifiable to make any claims that the difference here found between hydrogen and helium really represents completely the difference observed experimentally and I present the results merely as suggesting a possibility. There is a hope, however, that it may be possible, with these results as a basis, to find out something about the effect of exchanges of smaller amounts of energy experimentally. For there are a number of reactions, for example the decomposition of azomethane, in which we judge, from the pressure at which the rate constant begins to fall off, that all possible oscillators, including those of considerably lower frequency than 1000 cm.$^{-1}$, are involved. If it is true that the difference between hydrogen and helium indicates that quantum jumps of two vibrators simultaneously do not often occur, then the difference between the two gases should be much less in these cases where transfers of much smaller amounts of energy are possible without the double jumps occurring. Unfortunately Ramsperger[31] has found that hydrogen seems to react with azomethane; nevertheless, it would be very interesting to try the effect of helium, as we may guess it would be appreciably greater than in the case of the ethers. But even in the case of the ethers, and assuming that the double jumps do not occur, it is evident, if the theory here presented is at all correct, that helium should have an appreciable, even if small, effect—one which slightly more sensitive methods of experimentation should detect. If it should be detected, it would then be interesting to try neon with apparatus of the same sensitivity. Here the mass is great enough to cause it to be so poor an activator that no effect should be detectable even with the most sensitive apparatus possible to devise.

[31] Ramsperger, private communication.

Another experiment of extreme interest, should it become possible, would consist in the investigation of a hydrogen gas composed of the newly discovered heavier isotope of hydrogen. Some of the experiments indicated, Dr. D. V. Sickman and I hope to carry out shortly.

I wish to express my thanks to Dr. Sickman for assistance in some of the calculations.

INDEX OF SYMBOLS
The number gives the equation in or near which the symbol is defined

a	24	q	30	$v_{nm, n'm'}$	9	ν	21
a_{ij}	29a	r	1	V	2	ν_0	1
A, A'	13, 18	r_∞	5	W, W_{nm}	7, 3	$\xi_1, \xi_2, \ldots \xi_q, \xi_i$	29a
b	24	r_0	14	W_1, W_2	49	ρ, ρ_i	17, 34
b_{ji}	29b	r_k	55	x	1	σ, σ_i	23, 35
B, B'	13, 18	$R_{nm}, R_{n'm'}$	3, 10	$x_1, x_2, \ldots x_q, x_j$	29a	$\phi, \phi_n, \phi_{n'}$	1
c	24	S	24	z	20	$\phi_n^i(\xi_i)$	32
C, C_k	11, 58	$T_{nm}, T_{n'm'}$	3, 10	α	11	χ_1, χ_2	46
$E, E_n, E_{n'}$	1	T_1, T_2	54	β, β_i	12, 36	ψ_{nm}, ψ	4, 7
G_1, G_2, G_k	51, 55	u_k	55	$\gamma_{nm, n'm'}$	8	ω	47
K	5	$u_{nn}, u_{n'n'}$	2, 10	γ_{12}	50		
m, m_j	1, 30	$u_{nn'}$	10	$\epsilon_{nm}, \epsilon_{n'm'}$	5, 8		
M	3	u_∞, u_∞'	13, 18	μ	22		
p_{12}	50	U_1, U_2, U_k	48, 49	μ_i	30		

§9. Summary

The rate constants for many unimolecular gas reactions decrease at low pressures, as the number of activating collisions becomes small. In a number of decompositions of organic compounds addition of sufficient hydrogen restores the rate constant to its high pressure value, the hydrogen being able to cause activation. Helium, however (in common with a number of other gases), apparently does not have this ability.

In order to gain a better understanding of these phenomena, an attempt has been made in the present paper to investigate the dynamics of energy exchange between organic molecules of the type which undergo decomposition in the gas phase and other simple molecules, in particular hydrogen and helium, which may activate or deactivate the organic molecules. Deactivation of an organic molecule may take place, for example, if some of its vibrational energy is changed into translational energy of the colliding atom or molecule. The calculations are based essentially on a simple one-dimensional model in which it is assumed that a particle collides with an oscillator along the line in which the latter is vibrating; some discussion has been given, however, of the modifications which should be introduced on account of the complexity of the organic molecule. The first calculations have been made on the basis of the Born collision method; since it was found, however, that probabilities of energy exchange greater than 1 occurred, a modification was introduced, following

recent work of the writer, and of London, which allowed an approximate calculation for large perturbations. It was still found that the probability that hydrogen should deactivate an activated molecule was such as to be consistent with the assumption that an activated molecule is deactivated every time it hits an unactivated molecule of the same kind, within a factor of around ten (this conclusion being drawn after a discussion of experimental results which give the relative probability that a hydrogen molecule and an unactivated molecule of the same kind will deactivate the activated molecule).

The various factors which affect the probability of transfer of energy have also been investigated. It was found that, in general, increasing the frequency of the oscillator decreases the probability, increasing the force constant of the oscillator decreases the probability, increasing the "sharpness" of the collision (i. e., the steepness with which the force between the oscillator and the colliding particle goes up as they approach) increases the probability, and increasing the mass of the colliding particle decreases the probability. The latter effect was of interest in connection with the observed difference between hydrogen and helium, and a study was made of the effect of the mass of the colliding particle when other things were varied. However, on account of various complications, it was not possible to decide whether the observed difference between hydrogen and helium actually found a complete explanation in the calculated results.

Note added in proof, Oct. 17, 1932.—Since this article was submitted Jackson and Mott, Ref. 10, have shown how to solve the differential equation 3 and evaluate the integral in (10), for the particular case, $\rho = 1$, when u_{nn} is left in the exponential form instead of being put in the form (13). A few rough calculations made from their formula seem to show about as satisfactory agreement with Table III as is shown between Tables I and II.

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THE VELOCITY AND MECHANISM OF RACEMIZATION. II. MANDELIC ACID

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As a continuation of the work described in Part 1,[1] we have investigated in a similar manner the racemization of mandelic acid in the presence of acid and alkali. The apparatus and methods are described in Part 1.[1] We chose mandelic acid in contrast to Rochelle salt, because the mechanism must necessarily be simpler, in so far as there is no possibility of meso formation. We supposed, as a result of our work already described, that complex formation was a necessary condition of racemization, but we have

[1] Campbell and Campbell, THIS JOURNAL, 54, 3834 (1932).