

## The Absolute Rate of Homogeneous Atomic Reactions

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## The Absolute Rate of Homogeneous Atomic Reactions

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The absolute rate of the recombination of three hydrogen atoms is calculated entirely theoretically. The manner in which rotation determines the dimensions of the activated complex in cases having little or no activation energy is discussed. The theoretical data are in good agreement with the experimental rates of Steiner and of Amdur. An immediate consequence of the theory is that energy trans-

fer occurs most effectively among particles which can react with each other, free atoms being more efficient than molecules. A qualitative application of potential surfaces to the problem of energy transfer as met in velocity of sound experiments and in experiments on maintenance of high pressure rates of unimolecular reactions is made.

### INTRODUCTION

IN previous papers<sup>2</sup> there has been developed and applied a theory of the rates of homogeneous reactions which takes explicitly into account the behavior of all the degrees of freedom of the reacting system. In order to evaluate exactly the expressions that are obtained it is necessary to construct a potential energy surface for the system. In the applications that have already been made<sup>2(b, c)</sup> this was not feasible and it was necessary to obtain approximate information about the surface from the data of spectroscopy. For diatomic and triatomic systems, however, it is possible to construct a surface which is in agreement with experimental data.<sup>3</sup> In this paper we shall show that from such surfaces one can calculate rates of reaction agreeing with experiment. From the surfaces considerable information is obtained concerning the mechanism by which energy is transferred during the three-body collisions by which atomic recombinations take place.

We shall consider in detail the reaction  $H+H+X \rightarrow H_2+X$ . Before proceeding to this case, we first consider atomic reactions of the type  $A+B \rightarrow AB$ . Although this reaction is very improbable, it is of great interest because from an investigation of the properties of the potential surface one learns how to take into account the relative angular momentum of two bodies which are going to react and also what is meant by the

collision diameter for such a reaction. This information can be carried over to associations of diatomic or polyatomic molecules in which there is no activation energy.

These results are of interest also in connection with the important work of Pelzer and Wigner<sup>4</sup> who took less explicit account of the fact that molecules usually approach with relative angular momentum.

### THE REACTION $AB \rightarrow A+B$

The general equation for the rate of any reaction is<sup>5</sup>

$$k_i = \kappa (F_a' / F_n) (kT/h) e^{-E_0/RT}. \quad (1)$$

This equation gives the concentration of the systems at a saddle point on the surface times the rate at which they are crossing the barrier times the probability ( $\kappa$ ) that once they cross the barrier they do not recross it. The usual potential energy surface for two atoms (Morse curve) is two-dimensional and it has no saddle point (maximum) except at infinity. It would seem as if Eq. (1), therefore, could not be applied. We must, however, remember that the Morse curve gives the energy of a system of two atoms as a function of the distance between them only for the case in which the atoms are approaching along the same straight line. In general this situation will not be encountered;

<sup>1</sup> Parker Traveling Fellow of Harvard University, 1934-5.

<sup>2</sup> (a) Eyring, *J. Chem. Phys.* **3**, 107 (1935). (b) Gershinowitz and Eyring, *J. Am. Chem. Soc.* **57**, 985 (1935). (c) Wynne-Jones and Eyring, *J. Chem. Phys.* **3**, 492 (1935).

<sup>3</sup> Eyring and Polanyi, *Zeits. f. physik. Chemie* **B12**, 279 (1931).

<sup>4</sup> (a) Pelzer and Wigner *Zeits. f. physik. Chemie* **B15**, 445 (1932). (b) Pelzer, *Zeits. f. Electrochemie* **39**, 608 (1933). (c) Wigner, *Zeits. f. physik. Chemie* **B19**, 203 (1932).

<sup>5</sup> Reference 2(a) Eq. (10). In accordance with the notation used in reference 2(c),  $\kappa$  has been substituted for  $\epsilon$ , the transmission coefficient, in order to avoid confusion with concentration.

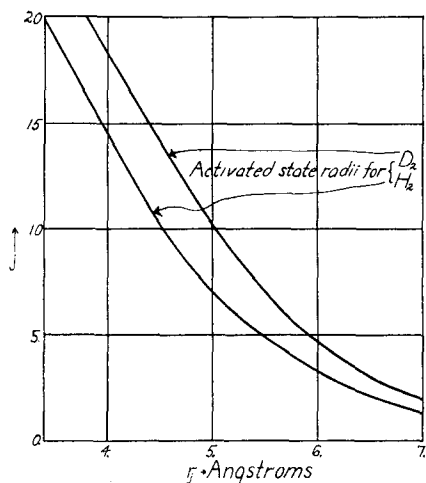


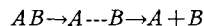
FIG. 1. The distance between the atoms in the activated state in the bimolecular association of  $H_2$  and  $D_2$ .

the atoms will have a relative angular momentum, which may be considered as a rotation in two degrees of freedom. The kinetic energy of rotation for each quantum state and for each interatomic distance must be added to the potential energy arising from electronic interaction, the latter being given by the Morse curve. The sum gives the energy that must be used in the exponential of the partition function, if we take as our zero of energy, for both the activated and normal states, the energy of the nonrotating molecule in its lowest vibrational state. For the case of two atoms we then have the activation energy  $E_0$  equal to  $D$ , the energy of dissociation. Now the addition of the energy

of rotation to the rest of the energy of the molecule will cause a shift in the position of the activated state. For the dissociation of a diatomic molecule with no rotation there is no maximum, so that the activated state is at infinity. When we have a rotating molecule we do get a maximum and as the energy of rotation increases the distance  $r_i$  at which the maximum occurs becomes smaller. (See Fig. 1. These curves have meaning only for the integral values of  $J$ , the rotational quantum number.)

This maximum locates the position of the activated state for the corresponding value of the rotational quantum number  $J$ . Knowing this we may calculate the activation energy for each value of  $J$  and by summing over all  $J$ 's we obtain the rotational partition function. Because of the Boltzmann factor, rotational states of very high energy are weighted out, so that at each temperature, for the association of two atoms there is an apparent collision diameter not very different from that for the collision of two diatomic molecules of the same kind. By differentiating with respect to  $r$  the total energy  $E = E_{vib} + E_{rot}$  for each value of  $J$  and setting this derivative equal to zero, we find  $r_i$ , the separation between the atoms in the activated state for the corresponding rotational quantum number. Fig. 1 gives the plot of  $r_i$  against  $J$  for  $H_2$  and  $D_2$  at  $300^\circ K$ .

The activated state for the dissociation of a diatomic molecule thus lies at the top of a different maximum for each value of  $J$ . For the specific rate  $k_1$  of the reaction



we then have:

$$k_1 = \frac{g_a i_a \kappa (2\pi(m_1 + m_2)kT)^{3/2} h^{-3} \sigma_a^{-1} \sum_{J=0}^{\infty} (2J+1) \exp \{ -(J(J+1)h^2(8\pi^2\mu r_i^2)^{-1} - (D - E_v))(kT)^{-1} \} kTh^{-1} \exp \{ -D(kT)^{-1} \}}{g_n i_n (2\pi(m_1 + m_2)kT)^{3/2} h^{-3} (1 - \exp \{ -h\nu(kT)^{-1} \}) \sigma_n^{-1} \sum_{J=0}^{\infty} (2J+1) \exp \{ -J(J+1)h^2(8\pi^2\mu r_0^2 kT)^{-1} \}} \quad (2)$$

$= LM^{-1}$  where  $L$  and  $M$  are the numerator and denominator, respectively, of the preceding fraction. For the reverse reaction

$$k_2 = L \{ (2\pi m_1 kT)^{3/2} h^{-3} (2\pi m_2 kT)^{3/2} h^{-3} g_n i_m \}^{-1}. \quad (3)$$

$\kappa$  is the transmission coefficient, i.e., the fraction of systems which, having crossed the maximum, do not return,  $m_1$  and  $m_2$  are the masses of the atoms in the molecule;  $\mu = m_1 m_2 / (m_1 + m_2)$ ;  $\sigma_a$  and  $\sigma_n$  are the symmetry numbers

of the activated and normal states, respectively.  $\nu$  is the vibration frequency of the molecule.  $i_a$ ,  $i_n$  and  $i_m$  are the statistical weights due to nuclear spins and remain equal since ortho and para forms are always present in equilibrium amounts; however, for the statistical weights of electronic states we have  $g_a = g_n = 1$  and  $g_m = 4$ .

The zero of energy is chosen to correspond to the nonrotating molecule in its lowest vibrational state; hence  $D$  is the energy of dissociation from this level to the asymptote of the Morse curve.  $E_V$  is the energy of vibration measured from the lowest vibrational state as taken from the Morse curve at the activated point  $r_j$  for each  $J$ . The rotational term in the denominator of (2) involves the constant  $r_0$ , the equilibrium separation of the atoms in the normal molecule, so that this moment of inertia is not a function of  $J$ . (We neglect the small interaction of vibration and rotation.) Thus at reasonably high temperatures we can replace this summation by  $8\pi^2\mu r_0^2 kT (\sigma_n h^2)^{-1}$ . The rotational partition functions for the normal and activated states of  $H_2$  and  $D_2$  at 500°K are given with considerable accuracy by the areas under the appropriate curves of Fig. 2. (The true curves are steplike.) The maxima of these curves give the most probable  $J$ 's for this temperature. With these most probable  $J$  values we can calculate the most probable values of  $\bar{r}_j$  (the collision diameter). A more useful average  $\bar{r}_j$  can be obtained from the equation

$$8\pi^2\mu r_j^2 kT h^{-2} = \sum_{j=0}^{\infty} (2J+1) \exp \{ -(J(J+1)h^2(8\pi^2\mu r_j^2)^{-1} - (V-E_V))(kT)^{-1} \}. \quad (4)$$

We find that for hydrogen  $\bar{r}_j = 4.4\text{\AA}$  and  $\bar{r}_j = 4.8\text{\AA}$ ; for deuterium  $\bar{r}_j = 4.1\text{\AA}$  and  $\bar{r}_j = 4.9\text{\AA}$ . For  $Cl_2$  and  $Br_2$  one gets  $r_j$ 's of the same order of magnitude. In general, if the association of two particles, atoms or radicals, requires no activation energy the apparent collision diameter, corresponding to the dimensions of the activated state, will be determined by the relative angular momentum, and at room temperature will be from 4 to 5 $\text{\AA}$ . We have applied this generalization in our treatment of trimolecular reactions.<sup>2b</sup>

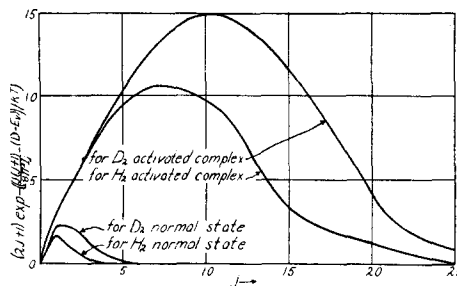


FIG. 2. Weighted number of states for each value of  $J$ . In normal state  $D = E_0$ . (Bimolecular association.)

From Eqs. (2a) and (2b) we can now calculate the rates of bimolecular association and unimolecular decomposition of  $H_2$  and  $D_2$ . If we assume that  $\kappa$  is the same for the reaction of  $D_2$  and  $H_2$  for  $H_2$  we find

$$k_1 = \kappa 3.6 \times 10^{14} e^{-D/RT} \text{ sec.}^{-1}, \\ k_2 = \kappa 2.78 \times 10^{14} \text{ cm}^3 \text{ moles}^{-1} \text{ sec.}^{-1},$$

and for  $D_2$

$$k_1 = \kappa 3.61 \times 10^{14} e^{-D/RT} \text{ sec.}^{-1}, \\ k_2 = \kappa 1.99 \times 10^{14} \text{ cm}^3 \text{ moles}^{-1} \text{ sec.}^{-1}.$$

The transmission coefficient  $\kappa$  is something like  $10^{-14}$  instead of being of the order unity as it frequently is when no non-adiabatic process is involved.<sup>6</sup>

We see that  $H_2$  and  $D_2$  decompose unimolecularly at the same rate except for the difference in zero-point energy. This is because the mass factors cancel out in the general equation for the rate and in addition the ratio  $F_{rot}^*/F_{rot}$  is the same for  $H_2$  and  $D_2$  although the individual rotational partition functions for the activated and normal states ( $F_{rot}^*$  and  $F_{rot}$ ) for  $H_2$  are quite different from those for  $D_2$ . We also note that the rate  $k_2$  for the unimolecular association of hydrogen atoms is nearly  $(2)^{1/2}$  times the rate of association of deuterium. This is to some extent fortuitous, since it arises from the cancellation of a number of terms. This ratio of  $2^{1/2}$  for the relative rates strikingly exemplifies the

<sup>6</sup> For an excited diatomic oscillator with a reasonable sized dipole the interval before radiation is frequently around  $10^{-2}$  sec. In the case of hydrogen, where there is no dipole but only a quadrupole moment, we should expect a mean life of the order of seconds, so that  $\kappa$  may well be as small as  $1/\nu \approx 10^{-14}$ .

fact that one is not justified in postulating simple mechanisms or rate expressions on the basis of a single numerical agreement.

The reason that the bimolecular association of the atoms plays a negligible role in the actual process of recombination is that  $\kappa$  is so very small. The usual assumption will be shown to be correct that at atmospheric pressure about every thousandth collision among atoms is a three body one and forms a stable molecule whereas only about every  $10^{-14}$  diatomic collision is stabilized by radiating energy.

#### THE REACTION $A+B+C \rightarrow AB+C$

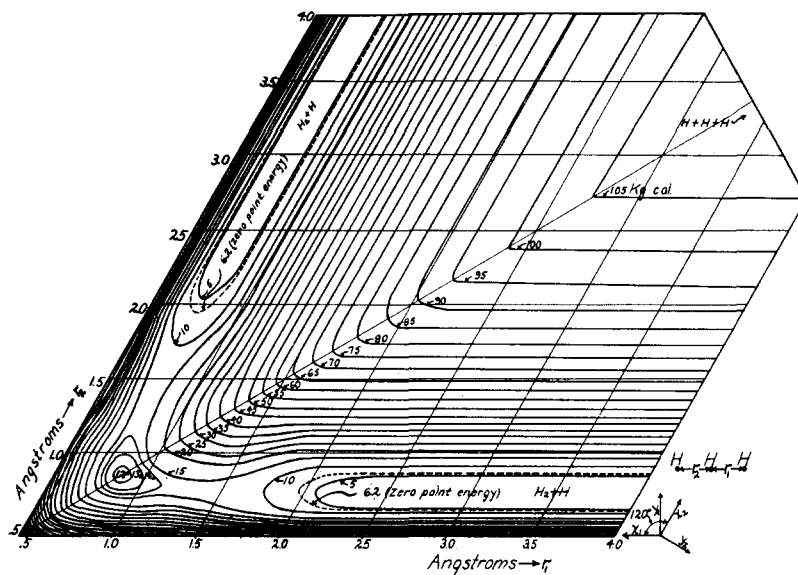
We first consider the case in which  $A$ ,  $B$  and  $C$  are all hydrogen atoms. A system of three atoms has nine degrees of freedom. In the normal state all these are free translations. In the activated state we have a triatomic quasimolecule. For three hydrogen atoms for all except very large distances the configuration of lowest potential energy is that in which all three atoms lie on the same straight line. This important type we discuss first. The other important type to be treated later is the isosceles triangle configuration for the activated complex. The nine normal coordinates of the linear complex are three of translation of the system as a whole, two of rotation of the system, two for bending vibrations and two for motions along the straight line. We make the usual assumption that the two rotations and three translations are separable from the four internal coordinates. Of the four internal coordinates there are two transverse vibrations of equal frequency. Upon writing out in full the potential energy for the system the two transverse vibrations are seen to be separable from the two motions along a straight line up to terms involving the fourth power of the bending angle. Because this interaction is so small it is principally the transfer of energy between the two remaining degrees of freedom which is responsible for the stabilization (or dissociation) of the diatomic molecule by the third body. These last two degrees of freedom then are those which we now investigate.

Eyring and Polanyi<sup>3</sup> in collaboration with Wigner have shown how to construct a potential energy surface for three collinear atoms such

that the classical motion of a mass point on this surface will describe the behavior of the system. Such a surface for 3H atoms is shown in Fig. 3.  $r_1$  represents the distance between atoms 1 and 2 and  $r_2$  the distance between atoms 2 and 3. The contour lines are equipotentials spaced at intervals of 5 kg.cal. Both Figs. 3 and 4 were constructed in the usual way<sup>3</sup> with 14 percent Coulombic energy and the following constants for the Morse curve for hydrogen: heat of dissociation = 102.4 kg.cal.; vibration frequency  $\omega_0 = 4375$  cm<sup>-1</sup>;  $a = 1.94 \text{ \AA}^{-1}$ ;  $r_0 = 0.74 \text{ \AA}$ . This surface has many features in common with other surfaces which represent the interactions of three atoms, any two of which can form a diatomic molecule. The angle that the axes make with each other is always 60° for three like atoms; otherwise it is a function of the relative masses.<sup>3</sup> For any set of three atoms the surface will have the same general appearance. In particular, for the regions of high potential energy, in which we shall be principally interested, the surfaces are divided by some line into two regions, each of which is developable, i.e., the energy in each may be expressed as the sum of two potentials each depending on a single coordinate.<sup>7</sup> It is this feature which enables us to discuss simply the transfer of energy between the two degrees of freedom associated with the two distances  $r_1$  and  $r_2$  and to determine the probability that a system with a given amount of energy will react. These two degrees of freedom of the linear molecule fix the relative translation of the three atoms. In what follows, for the sake of definiteness, we shall refer to the hydrogen surface shown in Fig. 3 in which the dividing line is  $r_1 = r_2$ . The behavior of other systems of three atoms which can form diatomic molecules is entirely analogous. The cases in which one of the atoms is an inert gas or in which the catalyzing particle is a molecule will be discussed later.

Although the surface is somewhat approximate in the region of low potential energy it is much more accurate for energies greater than 45 kg.cal.

<sup>7</sup> See for example Kimball and Eyring, J. Am. Chem. Soc. **54**, 3381, etc. (1932) Figs. 1, 2, and 3 in which this feature is to be observed. In these particular cases, as well as for the three hydrogen atoms, the line makes equal angles with the coordinates  $r_1$  and  $r_2$ .

FIG. 3. Energy contour map of linear  $H_3$  molecule.

per mole. We shall see that the greater part of the systems that associate (or dissociate) cross the line  $r_1=r_2$  in the region of high potential energy, so that the part of the surface that is inexact does not enter into our calculations. The calculations in the section immediately following depend only on that portion of the surface corresponding to potential energies greater than 45 kg.cal.

The section of the surface to the right of the line  $r_1=r_2$  is developable in terms of the Cartesian coordinates  $x_1$  and  $y_1$ . The part to the left and above  $r_1=r_2$  is developable in terms of the Cartesian coordinates  $x_2$  and  $y_2$ , the latter of which is taken perpendicular to the axis  $r_2$ . The angle between  $y_1$  and  $y_2$  and between  $x_1$  and  $x_2$  is then  $120^\circ$  (see Fig. 3). The energy of the mass point representing the system when it is in the first region is

$$\frac{1}{2}u(\dot{x}_1^2 + \dot{y}_1^2) + V(x_1, y_1), \quad (5)$$

$$\text{where } \dot{x} = \frac{dx}{dt} \text{ etc.}; \quad u = \frac{(m_1 + m_2)m_3}{m_1 + m_2 + m_3} = \frac{2}{3}m$$

for our hydrogen atoms.<sup>8</sup> Similarly, in the upper part of the surface the energy is

$$\frac{1}{2}u(\dot{x}_2^2 + \dot{y}_2^2) + V(x_2, y_2).$$

Along the line  $r_1=r_2$  we have the relation

$$y_2 = 0.5y_1 + 0.866x_1. \quad (6)$$

This relation expresses the physical fact that suddenly as  $r_1$  becomes equal to  $r_2$  motion within the system which was pure translation becomes redistributed between vibration and translation. This redistribution also takes place in the vibrational energy. This abrupt change in developability in one set of coordinates to developability in another probably often holds in ordinary molecules where there is no internal translation. Where this is found to be so it will provide a very convenient means of discussing many problems. Let us now suppose that in the  $x_1, y_1$  valley

<sup>8</sup> See Eyring and Polanyi, reference 3, Fig. 16 and accompanying text. Their coordinates  $-b$  and  $g$  correspond to our  $x_1$  and  $y_1$ . We should also like to mention that in their Eq. (25) on p. 307  $\sin \varphi$  should be replaced by  $-\sin \varphi$ . Accordingly, the angle between  $b$  and  $c$  in Fig. 17 should be taken as  $60^\circ$ , as we have done in our Fig. 3, where  $r_1$  and  $r_2$  correspond to  $b$  and  $c$ , respectively. We are indebted to Dr. O. K. Rice for kindly pointing out this error in sign.

there is a system (mass point) whose total energy is greater than  $108.6 + R(J)$  kg.cal., where  $R(J)$  is the rotational energy corresponding to the angular momentum of the entire system. (This  $R(J)$  creates a ridge along the edge of the valleys converting the central plateau into a shallow basin, in the same manner as it forms the maximum of the potential energy curve for the diatomic molecules, which case we have discussed above.) If the point representing our system is to remain in the valley (in spite of having the energy  $108.6 + R(J)$ , which is enough to dissociate it), this energy must be distributed in the  $x_1$  and  $y_1$  directions in such a way that the part of it in the  $y_1$  direction,  $\frac{1}{2}m\dot{y}_1^2 + V(x_1, y_1)$ , is less than  $108.6 + R(J)$  kg.cal. Since the surface is developable in this region we can have no transfer of energy between the  $x_1$  and  $y_1$  directions, so that the system cannot dissociate before it reaches the median line. When the mass

point reaches this line it will pass into the other valley, since along the part of this line where  $V(r_1, r_2) = 45$  kg.cal. (which is the region we are considering) no activation energy is needed, as the surface shows. As soon as it crosses this line the energy will be developable in terms of the coordinates  $x_2, y_2, \dot{x}_2$  and  $\dot{y}_2$  where  $\dot{y}_2$  is given by Eq. (6). We see, therefore, that there is a definite probability that enough energy will be transferred to the  $y_2$  direction to make the system dissociate, i.e., cross over the ridge of the valley onto the plateau and remain there. By the principle of microscopic reversibility, this will also give us the probability that a system of three atoms will react to give a molecule and an atom. This is the reverse reaction in which we are, of course, also interested.

There remains only the formal problem of setting up the required probability integral. We first consider

$$H = h^{-2} \int_a^b dx \int_c^d dy \int_e^f dp_x \int_k^l dp_y \exp - \{ (\frac{1}{2}u(\dot{x}_1^2 + \dot{y}_1^2 + V(x, y)) (kT)^{-1} \} \quad (7)$$

where  $h^{-2}$  is the normalization factor. We determine the limits  $a, b, c$ , etc., in the following manner. We are interested in the fraction of systems for which

$$\frac{1}{2}u(\dot{x}_1^2 + \dot{y}_1^2) + V(x_1, y_1) > 108.6 + R \quad (8)$$

and at the same time

$$\frac{1}{2}u\dot{y}_2^2 + V(x_1, y_1) > 108.6 + R, \quad (9a)$$

which, by (6), becomes

$$\frac{1}{2}u(0.5\dot{y}_1 + 0.866\dot{x}_1)^2 + V(x_1, y_1) > 108.6 + R. \quad (9b)$$

There are the additional conditions

$$0 < \dot{x}_1 < \infty \quad (10)$$

and

$$0 < \frac{1}{2}u\dot{y}_1^2 + V(x_1, y_1) < 108.6 + R, \quad (11)$$

which restrict the systems considered to the valley. These four conditions taken together restrict us to the fraction of systems originally composed of a molecule and an atom in the  $x_1, y_1$  valley which dissociate into three atoms after crossing into the  $x_2, y_2$  valley. These conditions give the upper and lower limits of the probability integral  $H$ . The two strongest conditions are (9b) and the second inequality in (11) which we

will call (11b). (11b) gives the upper limit for  $\dot{y}_1$

$$\dot{y}_1 = (2(108.6 + R - V))^{1/2} u^{-1/2} = g.$$

From (9b) we can obtain the lower limit for  $\dot{y}_1$ ; for, solving, we get

$$\dot{y}_1 = 2g - 1.732x_1 = 2g - 3^{1/2}g.$$

But this is the lower limit only until  $\dot{y}_1 = -g$ , otherwise condition (11b) would not be fulfilled. Letting  $\dot{y}_1 = -g$  and solving for  $\dot{x}_1$ , we get  $\dot{x}_1 = 3^{1/2}g$ . There is also a lower limit on  $\dot{x}_1$ , since  $\dot{y}_1$  cannot be greater than  $g$ , i.e.,  $\dot{x}_1 = g3^{-1/2}$ . We can, therefore, divide our space into two regions, in one of which

$$2g - 3^{1/2}x_1 \leq \dot{y}_1 \leq g \quad \text{and} \quad g3^{-1/2} \leq \dot{x}_1 \leq 3^{1/2}g; \quad (I)$$

and in the other

$$-g \leq \dot{y}_1 \leq g \quad \text{and} \quad 3^{1/2}g \leq \dot{x}_1 \leq \infty. \quad (II)$$

If we replace the coordinates  $x$  and  $y$  by the coordinates  $\xi$  measured along the line  $r_1 = r_2$  and  $\eta$  perpendicular to this direction, our potential at the activated state can be written as a function of  $\xi$  alone, to a good approximation. The rate with which the reaction proceeds is given by the density in phase space of the points representing

the reacting system per unit of length normal to the line  $r_1=r_2$  multiplied by the velocity of these points in the  $\eta$  direction. Since we can neglect the small dependence of the potential upon  $\eta$  the integral over unit length  $\int_{-1}^1 d\eta$  simply yields unity. The limits of the integral over  $\xi$  as well as the potential along this line  $r_1=r_2$  are dependent on the amount of rotation and therefore upon the quantum number  $J$  for this linear symmetrical activated complex. For  $J=0$  corresponding to no rotation an interesting situation arises. To get the number of molecules formed we should integrate  $\xi$  from  $r_1=r_2=0$  to  $r_1=r_2=l$  where  $l$  is of the order of a mean free path, since at this distance the attractive potential will have a maximum due to external perturbations. Actually if all such collisions resulted finally in the formation of a stable molecule we should get a very large rate of combination. We must, however, consider the subsequent fate of the diatomic molecule formed with such a very large amplitude of vibration, i.e., the corresponding  $\kappa$ . A subsequent collision normal to this axis will almost certainly decompose the molecule whereas a collision in the direction of the axis is apt to

stabilize it. Thus the chance that the molecule will persist after the next collision is approximately  $d/l$  where  $d$  is a normal atomic collision diameter and  $l$  is the length of the molecular axis (the mean free path). We should, therefore, (when  $J=0$  as for other cases) use approximately  $d$  rather than the mean free path  $l$  as the upper limit in the phase integral (7) (if  $\kappa$  is to be taken as approximately unity) since this integral is very nearly proportional to the upper limit.

Now instead of considering the surface for each value of  $J$  separately we use the surface for  $J=0$  and integrate out to  $r_1=r_2=4.4\text{\AA}$  which is the position of the rotation ridge separating the plateau from the valley for the average  $J$  at this temperature ( $300^\circ\text{A}$ ). This procedure introduces but little error since the potential surfaces change only slightly with  $J$  and even choosing the position of the rotation ridge  $1\text{\AA}$  too far out would only multiply the true rate by a factor of approximately 1.25. Underestimating the distance to the ridge by a similar amount underestimates the rate by a similar factor.

Introducing the limits of integration into (7) gives the equality

$$H = h^{-2} \int_0^{4.4 \times 10^{-10}} \exp \{-V(\xi)(kT)^{-1}\} d\xi \left[ \int_{z=0}^{3.1} \int_{-2.0}^{2.0} \exp \{-\frac{1}{2}\mu(\dot{x}^2 + \dot{y}^2)(kT)^{-1}\} \mu^2 d\dot{x} d\dot{y} \right. \\ \left. + \int_{z=0}^{\infty} \int_{-\infty}^{\infty} \exp \{-\frac{1}{2}\mu(\dot{x}^2 + \dot{y}^2)(kT)^{-1}\} \mu^2 d\dot{x} d\dot{y} \right].$$

We have evaluated this integral numerically. The region for which  $V(\xi)$  is less than 45 kg.cal. makes a negligible contribution. Even keeping the original assumption that the surface is ruled, the contribution along the line  $r_1=r_2$  near the minimum is unimportant. Now the fact that the minimum is higher than corresponds to such an assumption decreases still further the contribution to  $H$  from this region since it introduces an activation energy for particles crossing  $r_1=r_2$  near the minimum. We estimate the error made by neglecting the region where  $V(\xi) < 45$  kg.cal. to be not more than 10 percent. If we take for the zero the energy of three separated hydrogen atoms we find that  $H = 2\mu kT \cdot 1.64 \times 10^{-8}/h^2$ . It can be shown that if all systems crossing the line  $r_1=r_2$  with enough energy actually reacted, the corresponding partition function  $H'$  would be equal to  $2\pi\mu kT \cdot 4.4 \times 10^{-8}/h^2$ . The ratio  $H/H'$  gives us a measure of the transmission coefficient  $\kappa$ . We find that approximately  $\frac{1}{3}$  of the systems that cross the barrier with enough energy react. In this case there is only one degree of freedom which can take away the excess energy. Where there are more,  $\kappa$  will be larger, and for polyatomic molecules it will approach unity.

The rate of the association reaction  $k_3$  is therefore given by

$$k_3 = \frac{g_a i_a}{g_n i_n} \frac{8\pi^2 I^* kT (\sigma^* h^2)^{-1} \prod_{i=1}^2 (1 - \exp \{-h\nu_i(kT)^{-1}\})^{-1} (2\pi m^* kT)^{1/2} h^{-3} H \bar{v}}{(2\pi m kT)^{3/2} h^{-9}}, \quad (12)$$



where  $I^*$ ,  $\sigma^*$ ,  $\bar{v} = (kT/2\pi m^*)^{1/2}$  and  $\nu_i$  are, respectively, the moment of inertia, symmetry number, average velocity across the barrier and vibration frequencies of the activated complex;  $m$  is the mass of one of the atoms.  $g_{aia}(g_{ni}i_n)^{-1} = \frac{1}{4}$  exactly as for the bimolecular association. In this expression the most uncertain quantity is the moment of inertia of the activated complex, since the atoms may be from two to four Angstroms apart when they cross the line  $r_1 = r_2$ , and the distance  $l$  is also a function of  $J$ . We take as an average, as well as a most probable value,  $r_1 = 3A$ . This makes our maximum error a factor of two, although the probable error is much less. The one other uncertain quantity is the magnitude of the frequencies of the transverse vibrations. The absolute rate is not very sensitive to changes in this quantity, but without it we cannot predict the isotope effect with  $H_2$  and  $D_2$ . The evidence available seems to indicate that these frequencies should be somewhat lower than those given by surface IV. If we assume the frequencies are very low the vibration partition functions take the classical values  $kT/h\nu_i = kT2\pi m^{1/2}/hf_i^{1/2}$  and we get a factor of  $m$  from the two frequencies of the activated state. This  $m$  in the numerator with the  $m^{1/2}$  in the denominator of (9) gives an  $m^{-1/2}$  as the final dependence of the rate on the mass. This agrees with the results of Farkas<sup>9</sup> and with those of Amdur.<sup>10</sup> This agreement gives us some information about the values of the vibration frequencies that we must insert into Eq. (12). To give the classical mass dependence these frequencies must be of the order of magnitude of  $100\text{ cm}^{-1}$ . Using this frequency we get 7 as the numerical value of the partition function for the two transverse vibrations. Although the bending frequencies are low the one associated with  $\xi$  is sufficiently large to make the total zero-point energy approximately that of the normal state in agreement with the results of Farkas and of Cook and Bates.<sup>9</sup> Substituting in (12) the numerical values, we get  $k_3 = 3.1 \times 10^{15}\text{ cm}^6\text{ moles}^{-2}\text{ sec}^{-1}$ .

The process just considered involves the three atoms 1, 2 and 3, where 2 lies in between. Atom 3 comes up to the unstable configuration 1-2, atom 1 leaves and 2 and 3 form a stable

molecule. This mechanism accounts for those cases in which the atoms are moving along a straight line, or at such angles as are included by the amplitudes of the transverse vibrations of our activated state. When the amplitudes of these vibrations are very large, i.e., for atoms approaching at very sharp angles, it is no longer legitimate to make the assumption that the energy is still separable in terms of the coordinates that were good approximations to normal coordinates for the linear case. This being so it may be there is some second region of our many dimensional energy surface which is as effective as that just considered. Such a new region would make possible an additional mechanism for the reaction. We find that this situation actually arises for configurations in which one of the three atoms is moving perpendicular to the line forming the other two. The pair moving along the line reacts and the third carries off (or for the reverse process furnishes) the excess energy.

#### SECOND TYPE OF COLLISION FOR 3 H ATOMS

Fig. 4 is the potential energy surface for two hydrogen atoms moving along a straight line, the distance between them being  $r_1$  with the third hydrogen atom moving perpendicular to and toward (or away from) the center of this line. The distance from the third atom to the center of gravity of the first two is  $r_2$ . The three atoms thus always form an isosceles triangle. In Fig. 4 only a little more than half the surface is drawn as it is symmetrical about  $X=0$ . Here again we see that a line  $AB$  divides the surface into two regions in which different sets of coordinates are appropriate. In the region to the southeast of  $AB$  the most convenient coordinates are the parabolic cylindrical set,<sup>11</sup>  $u$ ,  $v$  and  $w$ , where

$$x = c(v - u); \quad y = 2c(uv)^{1/2}; \quad z = w.$$

In this coordinate system our equipotential lines are nearly the parabolas  $v = \text{const.}$  In the region to the northwest plane polar coordinates  $\rho$  and  $\theta$  with origin at the point  $c$  may be used and in this part of the surface the equipotentials are given to a good approximation by  $\rho = \text{const.}$

<sup>9</sup> Private communication.

<sup>10</sup> Amdur, J. Am. Chem. Soc. 57, 856 (1935).

<sup>11</sup> Adams, *Smithsonian Mathematical Formulae* (1922), p. 105.



to the plateau (which is associated with increasing reactivity) increases the transfer of energy between degrees of freedom.

#### COMPARISON WITH EXPERIMENTAL RESULTS

There is some disagreement as to the relative efficiencies of H and H<sub>2</sub> as third bodies in the recombination of hydrogen atoms. The work of Steiner indicates that H<sub>2</sub> is at least ten times as efficient. The work of Amdur gives contrary results. We can examine these relative efficiencies from the theoretical point of view which we have adopted. In order to have a hydrogen molecule transfer energy by an exchange of partners, it must lie between two atoms on a straight line. Thus we have the configuration H—H—H—H and reaction will occur when the central hydrogen molecule splits and we get two new ones formed. There are three factors which might make this process less probable than the reaction with three hydrogen atoms. The first is that there is less probability of finding the four atoms on a line than of finding three. The difference, however, is not as great as one might expect, for the rotational partition function of hydrogen is so small that the molecules will have the correct orientation about half the time. Secondly, one-third of those collisions in which the atoms are collinear will have the molecule between the two atoms. These combined probabilities would make the hydrogen molecule  $\frac{1}{3}$  as effective as the atom. The third factor that could reduce the efficiency would be the necessity of an activation energy for the approach of two hydrogen atoms to a hydrogen molecule. We can make no definite statement about this, since we have not calculated the necessary surface. We thus come to the conclusion that H<sub>2</sub> is at best  $\frac{1}{3}$  as efficient as H. This is in agreement with the results of Amdur rather than those of Steiner. Only if the transfer of energy between the rotation of the colliding H<sub>2</sub> molecule and the associating atoms is much greater than our present knowledge of the potential surface indicates could the calculated order of efficiencies be reversed.

The reasoning of the preceding paragraph

indicates why hydrogen molecules are so much more efficient than others for the transfer of energy. Other authors have assumed that it is because the mechanism is one of transfer of rotational energy to vibrational and that since hydrogen has such a small moment of inertia it can transfer a large amount of energy in a single quantum. From the preceding considerations it would seem that the efficiency of hydrogen may be due rather to the fact that it can so readily form a complex with the reacting substances, since its moment of inertia is so small that it is in a favorable configuration about half of the time at room temperature.

We see that in general, according to the point of view which has here been put forth, the ability to transfer energy is intimately connected with reactivity. This is in agreement with most of the available data. Franck and Eucken<sup>13</sup> have reached the same conclusions through more qualitative methods. Our calculation for the 3 H case shows how any other case may be treated quantitatively. The method is valid not only for actual chemical reactions but also in cases in which no bonds are formed or broken. Thus it can be applied to the data obtained in sound dispersion experiments, where all the data indicate that energy is most easily transferred among molecules that can react with each other.<sup>14</sup> The method may also be applied to the study of the maintenance of the high pressure rate of unimolecular reactions by foreign gases. Here too most of the observed facts are fitted by the theory. As we might expect, comparatively inert substances vary considerably in the efficiency with which they maintain the rate. This is shown by the work of Volmer and his collaborators on N<sub>2</sub>O.<sup>15</sup> Returning to the recombination of hydrogen atoms, Bonhoeffer<sup>16</sup> has made a qualitative determination of the relative effi-

<sup>13</sup> Franck and Eucken, *Zeits. f. physik. Chemie* **B20**, 460 (1933).

<sup>14</sup> Eucken and Becher, *Zeits. f. physik. Chemie* **B20**, 467 (1933); Kneser and Knudsen, *Ann. d. Physik* **21**, 682 (1935); Richards and Reid, *J. Chem. Phys.* **2**, 206 (1934).

<sup>15</sup> Volmer and Froehlich, *Zeits. f. physik. Chemie* **B19**, 89 (1932).

<sup>16</sup> Bonhoeffer, *Zeits. f. physik. Chemie* **119**, 385, 475 (1926).

ciency of various gases as third bodies. The order he finds agrees very well with the relative reactivities. The data of Senftleben and Hein,<sup>17</sup> however, are in definite disagreement with our theory, but the absolute rate for the recombin-

ation of hydrogen atoms found by these authors is very much lower than that of Amdur or Steiner.

The method of potential energy surfaces thus provides us with a clear picture of homogeneous catalytic processes. It forms a convenient basis for a satisfactory discussion of the problems of energy transfer.

<sup>17</sup> Senftleben and Hein, *Ann. d. Physik* **22**, 1 (1935).

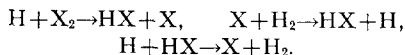
## A Summary of Experimental Activation Energies of Elementary Reactions Between Hydrogen and the Halogens

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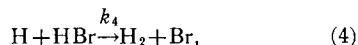
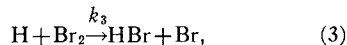
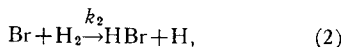
Existing experimental data on reactions between hydrogen and the halogens have been analyzed to give values of the activation energies of the intermediate reactions involved. These are compared with calculated values due to Eyring and Wheeler.

EVIDENCE has been accumulating over a period of years that reactions between molecules and free atoms may have appreciable activation energies. This evidence is in the main not direct, but must be deduced from considerations as to the most probable mechanism of reaction. In this paper the experimental evidence for reactions of hydrogen and the halogens is reviewed and tentative values of the activation energies are suggested. The reactions in question are of the types:



### HYDROGEN-BROMINE REACTIONS

This reaction system has been quite thoroughly covered in both its theoretical and experimental aspects by Kassel in his *Kinetics of Homogeneous Gas Reactions*. However, newer numerical data have made possible more exact conclusions as to the individual reactions. The chain consists of the steps:



which lead to the theoretical expression:

$$\frac{d[\text{HBr}]}{dT} = 2k_2(k_1/k_5)^{\frac{1}{2}} \frac{[\text{H}_2][\text{Br}_2]^{\frac{1}{2}}}{1 + k_4/k_3[\text{HBr}]/[\text{Br}_2]}.$$

From experimental researches by Bodenstein and Lind,<sup>1</sup> confirmed by Bach, Bonhoeffer and Moelwyn-Hughes<sup>2</sup>  $2k_2(k_1/k_5)^{\frac{1}{2}}$  and  $k_4/k_3$  have been determined. Since  $k_5/k_1 = K_D$ , the dissociation constant of bromine, which is now well known,  $k_2$  may be evaluated from the knowledge of  $2k_2(k_1/k_5)^{\frac{1}{2}}$ . The temperature coefficient of  $k_2$  will give  $A_2$ , the activation energy of reaction (2). If the data of Gordon and Barnes<sup>3</sup> on  $K_D$  are used, both sets of results yield  $A_2(\text{Br} + \text{H}_2) = 17.7 \text{ Kcal.}$

<sup>1</sup> Bodenstein and Lind, *Zeits. f. physik. Chemie* **57**, 168 (1907).

<sup>2</sup> Bach, Bonhoeffer and Moelwyn-Hughes, *Zeits. f. physik. Chemie* **B27**, 71 (1934).

<sup>3</sup> Gordon and Barnes, *J. Chem. Phys.* **1**, 792 (1933).