

## Calculation of the Rate of Elementary Association Reactions

E. Wigner

Citation: *The Journal of Chemical Physics* **5**, 720 (1937); doi: 10.1063/1.1750107

View online: <http://dx.doi.org/10.1063/1.1750107>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/5/9?ver=pdfcov>

Published by the AIP Publishing

---

### Articles you may be interested in

[On the calculation of reaction rate constants in the transition path ensemble](#)

*J. Chem. Phys.* **110**, 6617 (1999); 10.1063/1.478569

[Refined calculated ion–molecule association rates](#)

*J. Chem. Phys.* **72**, 5284 (1980); 10.1063/1.439769

[Note on the QuantumMechanical Calculation of Reaction Rates](#)

*J. Chem. Phys.* **21**, 2071 (1953); 10.1063/1.1698745

[Remarks on the Calculating Rates of Some Radical Reactions](#)

*J. Chem. Phys.* **19**, 256 (1951); 10.1063/1.1748183

[Entropy and the Absolute Rate of Chemical Reactions I. The Steric Factor of Bimolecular Associations](#)

*J. Chem. Phys.* **2**, 853 (1934); 10.1063/1.1749408

---



planes. Since the atoms do not occupy fixed lattice positions within a plane the Bragg equation cannot be used for calculation of the linear separation of the planes.

The proposed model for the structure in liquid benzene differs from the model employed by Katzoff<sup>4</sup> chiefly in the assumption that the molecules lie flat in planes. Katzoff employed a model based upon crystal structure, in which the molecules lie in planes 3.4Å apart and are tilted with respect to the plane. This difference is reflected in the atomic distribution curves obtained in the two cases. Although the  $q'(r)$  curve of Fig. 2 qualitatively resembles the distribution curve deduced by Katzoff, the two are not in the same units. Conversion to the same units gives curves which are not in quantitative agreement, although both curves show the double peak observed at 4–7Å in Fig. 2. This similarity is due to the assumption employed in both structures that neighboring molecules are oriented within a plane and that upper and lower planes contain molecules likewise oriented. Although the method

used here is a little more direct than the one employed by Katzoff the writer does not feel that the resolution obtained in x-ray scattering from a liquid is sufficient to enable one to make definite conclusions as to the uniqueness of either structure.

Katzoff and others have commented upon the bulge at the bottom of the first strong peak in the diffraction pattern (at  $s=0.3$ ). This bulge is also found in the diffraction pattern of benzene derivatives. In the corrected liquid scattering curve of Fig. 1 the bulge becomes relatively more prominent than in the total scattering. It is undoubtedly due, as suggested by Katzoff, to a predominance of interatomic distances of about 4Å—a condition which is caused by the orientation of neighboring flat molecules. The absence of this bulge in the diffraction pattern of cyclohexane and of long chain compounds supports this view.

The writer desires to express his appreciation to Professor W. H. Zachariasen for his helpful criticism.

## Calculation of the Rate of Elementary Association Reactions

E. WIGNER

*Department of Physics, University of Wisconsin, Madison, Wisconsin*

(Received June 18, 1937)

An upper limit for the rate of association reactions is found by determining the probability of a decrease of the relative energy of two atoms below zero energy, under the influence of a third body. The relation of this approximate calculation to the rigorous solution of the problem is discussed in Section 2. The results are applied to the recombination of  $J$  atoms, measured by Rabinowitch and Wood. Numerically, the agreement is quite good; however, the calculated values are somewhat too low, which cannot be explained by an inaccuracy of the method. Reasons for the discrepancy other than the possible nonadiabatic character of the reaction are discussed.

### 1

THE transition state method<sup>1</sup> allows the calculation of the rate of reactions which involve an activation energy. The assumptions which one has to make in order to apply this method are (1) that the reaction shall not involve a jump in the quantum state of the electrons,<sup>2</sup>

<sup>1</sup> Cf. for previous literature e.g. M. G. Evans and M. Polanyi, *Trans. Faraday Soc.* **31**, 876 (1935).

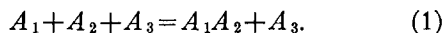
<sup>2</sup> The possibility of chemical reactions without quantum jumps in the state of the electronic system has been first realized by F. London, *Sommerfeld Festschrift* (S. Hirzel, 1928), p. 104.

(2) that classical mechanics be applicable to the motion of the nuclei (or that the ordinary way of taking into account quantum effects be justifiable) and, (3) that the number of systems crossing the activated state be the number of systems reacting. This last condition is always satisfied at sufficiently low temperatures and if the energy surfaces are not too complicated, the temperature at which their validity ceases will be rather high.<sup>3</sup> The common feature of the reactions to

<sup>3</sup> Cf. for a closer discussion of these conditions, E. Wigner, *Trans. Faraday Soc.* (1937).

which the transition state method can be applied in its usual form<sup>4</sup> is that the transition over a state with high energy be the rate determining step.

However, some of the most simple reactions, like the association of atoms to a molecule in a three-body collision, cannot be calculated by the present form of the transition state method, although its original form<sup>5</sup> embraces these reactions also. The purpose of the present note is the derivation of a formula for the rate of reactions of the type  $2J + A = J_2 + A$ , or



The assumption of the validity of classical mechanics which will be necessary in the present derivation also, is better fulfilled than for the reactions with activation energy. Also the exact shape of the energy surface enters much less critically, because there is no activation energy  $Q$ , and a calculation of the absolute rate is possible at least approximately. On the other hand, there is no limiting case in which the formula (1) to be derived here is a consequence of well-established principles of statistical mechanics. Such a limiting case existed for reactions with activation energy as that of very low temperature and sufficiently heavy masses to assure the validity of classical mechanics.

Eyring, Gershinowitz and Sun<sup>6</sup> have given a very ingenious method by which the rate of (1) can be rigorously calculated if the energy surface can be divided into two regions, both of which are developable. This is very nearly true for that part of the energy surface for the  $H + H + H = H_2 + H$  reaction which corresponds to the straight configuration of the atoms. However, it cannot be claimed that the majority of associations will proceed from a nearly straight configuration. For a bent configuration, the limits of the integration of Eq. (7) reference 6 should be changed and this will increase the probability of association for bent configurations. Eyring, Gershinowitz and Sun<sup>6</sup> tried to compen-

sate for neglecting to change the limits of their integral by considering the neighborhood of the isosceles triangle configuration also. Thus they counted some reactions twice, some not at all. This criticism of the very ingenious work of reference 6 should not be taken, of course, too seriously, since all that was claimed, and all that can be done at present, is to obtain the reaction rate within a not too large factor. That certainly has been accomplished by Eyring, Gershinowitz and Sun. The point was brought up partly to illustrate the point that an exact calculation of the rate of (1) is not feasible at present<sup>7</sup>—not even under simplifying assumptions for the energy surface—and partly to justify taking up the subject here again.

## 2

Theoretically,<sup>8</sup> of course, one could obtain the rate of (1) by considering the macrocanonic assembly of systems, containing an  $A_1$ , an  $A_2$  and an  $A_3$  atom in a great box of volume  $v$ . One can consider then those systems which are in the dissociated state at present but will go over into the right side of (1) within a time  $t$ . Whether a point in phase space corresponds to the left or right side of (1), may be ambiguous if all three atoms are close. However, if  $t$  is sufficiently large, this ambiguity will extend to a very small proportion of all the systems reacting, most of the molecules formed will be sufficiently far away already from the third body to leave no doubt as to their associated character. On the other hand,  $t$  shall not be taken long enough to allow for a second collision, i.e.,  $t$  shall be small compared with the time between collisions but very long compared with the collision time.

The systems which will react before  $t$  will be contained in a region  $R_t$  of phase space. The ends of this region may be a little uncertain, but the total probability of  $R_t$  will be well defined. The

<sup>7</sup> This does not preclude the possibility of calculating the absolute rate of (1) more accurately than can be done in practice for reactions with activation energy. Although the transition state method should give nearly exact results for the latter, the parameters of the energy surface enter in such a critical way into the formulas that a calculation of the whole rate is hardly feasible at present. Cf. also reference 3.

<sup>8</sup> The second section serves only to establish the connection between the (impracticable) exact calculation of the rate and the approximate calculation of the ensuing sections.

<sup>4</sup> H. Eyring, J. Chem. Phys. 3, 107 (1935); M. G. Evans and M. Polanyi (reference 1).

<sup>5</sup> M. Polanyi, Zeits. f. Physik 1, 90 (1920). The first complete outline of the theory has been given in R. Tolman's *Statistical Mechanics* (Chemical Catalog Co., 1927). Cf. also K. F. Herzfeld, *Kinetische Theorie der Wärme* (Müller-Pouillet's *Handbuch der Physik*, second edition, 1925).

<sup>6</sup> H. Eyring, H. Gershinowitz, C. E. Sun, J. Chem. Phys. 3, 786 (1935).

rate constant  $k$  is this probability, divided by  $t$ .

As we increase  $t$  (keeping it still below the time between two three-body collisions),  $R_t$  will assume the form of a longer and longer tube in phase space. We can put a surface  $S$  across this tube and  $k$  will be the number of systems crossing  $S$ . It does not matter where the surface  $S$  lies, it only must have no wrinkles which could be crossed by the same system twice. All the systems will cross  $S$  in the same direction.

The number of decomposing systems can be counted in a similar way. Furthermore, the continuation of  $S$  may be taken for the surface for this counting. If we do this, and still allow no wrinkles in  $S$ , the number of systems crossing it in one direction will be the number of associations, the number crossing it in the other direction, the number of dissociations (which, naturally, must be equal to the number of associations). Apart from having no "wrinkles,"  $S$  can be quite arbitrary as long as it divides the whole phase space into two separate parts: those corresponding to the left and the right side of (1). If the distance of  $A_3$  is very great from  $A_1$  and  $A_2$ ,  $S$  must be the  $H_0=0$  surface, where  $H_0$  is the mutual energy (potential and kinetic) of  $A_1$  and  $A_2$ .

If the distance of the third atom is small, and one still would take  $H_0=0$  for  $S$ , this  $S$  could possibly show wrinkles. These wrinkles would correspond to the relative energy of  $A_1$  and  $A_2$  falling below zero and rising again above this value during the same collision. No association would result then, although, counting the crossings through  $S$  in one direction, one would count these crossings. However, one can define an  $H_0$  depending on all coordinates, such that  $H_0=0$  should have no wrinkles, i.e., no path in phase space shall cross it more than once during one collision. This  $H_0$  will be equal to the relative energy of  $A_1$  and  $A_2$  for great distance of the  $A_3$ , will be different from this, however, if  $A_3$  is near to  $A_1$  and  $A_2$ . It will divide the whole phase space in two distinct parts and it will have the property that the total number of paths crossing it is as small as possible. This latter condition does not, of course, determine  $S$  (and even less  $H_0$ ), but it determines that minimum number, which is the reaction rate  $k$ .

3

We shall calculate now the number of systems crossing the  $H_0=0$  surface in unit time. No special assumption concerning the position of this surface will be made in this section and the formulas (3) and (5) hold, therefore, quite generally. In the later sections, however,  $H_0$  will be interpreted (for every position of  $A_3$ ) as the energy of  $A_1$  and  $A_2$  in the coordinate system in which their center of mass is at rest. Formula (11) will give, therefore, only an approximate value (an upper limit) for the rate constant  $k$ .

If  $H$  is the total Hamiltonian, we have

$$\begin{aligned}\frac{dH_0}{dt} &= \sum_i \left( \frac{\partial H_0}{\partial q_i} \frac{dq_i}{dt} + \frac{\partial H_0}{\partial p_i} \frac{dp_i}{dt} \right) \\ &= \sum_i \left( \frac{\partial H_0}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial H_0}{\partial p_i} \frac{\partial H}{\partial q_i} \right) \\ &= \sum_i \left( \frac{\partial H_0}{\partial q_i} \frac{\partial (H-H_0)}{\partial p_i} - \frac{\partial H_0}{\partial p_i} \frac{\partial (H-H_0)}{\partial q_i} \right).\end{aligned}\quad (2)$$

Those systems will cross the  $H_0=0$  surface in the decreasing sense, which are nearer than  $(dH_0/dt)/|\text{grad } H_0|$  from it, provided  $dH_0/dt$  is negative. We have, therefore ( $Z$  is the total integral of  $e^{-H/kT}$  over phase space)

$$k = \frac{v^2}{Z} \int \frac{dH_0/dt}{|\text{grad } H_0|} e^{-H/kT} d\sigma, \quad (3)$$

where  $d\sigma$  is a surface element of the  $H_0=0$  surface and the integration has to be extended over the region in which  $dH_0/dt < 0$ .

This is simply the derivative of the integral

$$I(E) = - \int \dots \int_{\substack{H_0 < E \\ dH_0/dt < 0}} (dH_0/dt) e^{-H/kT} \cdot dq_1 \dots dq_n dp_1 \dots dp_n \quad (4)$$

with respect to  $E$  at the point  $E=0$

$$k = \frac{v^2}{Z} \left( \frac{dI(E)}{dE} \right)_{E=0}. \quad (5)$$

[The real  $k$  is (rigorously) the minimum value of this expression for such  $H_0(q_1, \dots, q_n, p_1, \dots, p_n)$  which go over into the proper energy of the two associating particles for a large distance of the

third body but are not everywhere necessarily equal to it.] The integral  $I(E)$  is to be extended over that region of phase space in which  $H_0 < E$  and also (2) is negative.

4

As an example, the rate of a simple reaction (1) shall be calculated where all  $A$  are atoms. The approximate  $H_0$  which shall be used will be (for every distance of the  $A_3$ ) the proper energy of the associating atoms. We shall use in what follows the following coordinates: the components the vector  $\mathbf{q}_{12}$  pointing from  $A_1$  to  $A_2$ , the components of  $\mathbf{q}_3$  connecting  $A_3$  with the center of mass of  $A_1$  and  $A_2$ , and finally the components of the vector  $\mathbf{Q}$  pointing to the center of mass of all three atoms. The corresponding momenta are  $\mathbf{p}_{12}$ ,  $\mathbf{p}_3$ ,  $\mathbf{P}$ ;

$$H_0 = \frac{1}{2m_r} \mathbf{p}_{12}^2 + V_0, \quad (6)$$

where  $m_r$  is the relative mass of the associating atoms  $1/m_r = 1/m_1 + 1/m_2$  and  $V_0(r_{12})$  is the potential energy  $V(r_{12}, r_{13}, r_{23})$  for  $r_{13} = r_{23} = \infty$ . Thus

$$H - H_0 = \frac{1}{2\mu} \mathbf{p}_3^2 + \frac{1}{2M} \mathbf{P}^2 + V - V_0, \quad (7)$$

where  $1/\mu = 1/(m_1 + m_2) + 1/m_3$  and  $M$  is the mass of all three atoms together.

We have then by (2)

$$\frac{dH_0}{dt} = -\frac{1}{m_r} (\mathbf{p}_{12}, \text{grad}_{12} (V - V_0)) \quad (8)$$

and,

$$I(E) = \int_{H_0 < E} \cdots \int (1/m_r) (\mathbf{p}_{12}, \text{grad}_{12} (V - V_0)) \cdot e^{-H/kT} d\mathbf{q}_{12} d\mathbf{q}_3 d\mathbf{Q} d\mathbf{p}_{12} d\mathbf{p}_3 d\mathbf{P}. \quad (9)$$

The integration over  $\mathbf{Q}$  gives the total volume  $v$  that over  $\mathbf{p}_3$  and  $\mathbf{P}$  gives  $(2\pi\mu kT)^{3/2} (2\pi M kT)^{3/2}$ . One can perform an orthogonal transformation for  $\mathbf{p}_{12}$  making  $p_{12x}$  parallel to  $\text{grad}_{12} (V - V_0)$ . The condition  $dH_0/dt < 0$  means that the scalar product in (9) is positive, i.e., that  $p_{12x}$  has the sign of the grad. The conditions  $H_0 < E$  means  $p_{12x}^2 + p_{12y}^2$

$+ p_{12z}^2 < 2m_r(E - V_0)$ . Thus (9) becomes

$$I(E) = (2\pi kT)^{3/2} v (\mu M)^{3/2} m_r^{-1} \int_{H_0 < E, p_{12x} > 0} d\mathbf{q}_{12} \int d\mathbf{q}_3 \int d\mathbf{p}_{12} \cdot p_{12x} |\text{grad}_{12} (V - V_0)| \cdot \exp(-\mathbf{p}_{12}^2/2m_r kT - V/kT).$$

The integration over  $p_{12x}$  can be performed immediately and that over  $p_{12y}$  and  $p_{12z}$  also if one introduces polar coordinates in the  $p_{12y}p_{12z}$  plane. One obtains

$$I(E) = (2\pi kT)^4 kT v m_r (\mu M)^{3/2} \cdot \int_{V_0 < E} d\mathbf{q}_{12} \int d\mathbf{q}_3 |\text{grad}_{12} (V - V_0)| \cdot \{\exp(-V/kT) - [1 + (E - V_0)/kT] \cdot \exp[-(E + V - V_0)/kT]\}. \quad (10)$$

For (5), we have to differentiate this with respect to  $E$ . Differentiating with respect to the limit of integration involves setting  $V_0 = E$  in the integrand, which vanishes hereupon. Differentiating inside with respect to  $E$ , setting  $E = 0$  and dividing by  $Z/v^2 = v(2\pi kT)^{3/2} (m_1 m_2 m_3)^{3/2}$  gives  $(m_1 m_2 m_3 = m_r \mu M)$

$$k = (2\pi m_r kT)^{-1} \int_{V_0 < 0} d\mathbf{q}_{12} \int d\mathbf{q}_3 \cdot |\text{grad}_{12} (V - V_0)| (-V_0/kT) e^{-(V - V_0)/kT}. \quad (11)$$

If the associating atoms are different and there are  $n_1$  and  $n_2$  of them in the volume  $v$ , and  $n_3$  of the third body, the number of effective collisions will be  $n_1 n_2 n_3$  times (11), i.e., the rate constant is given by (11). If the associating atoms are identical and their number  $n$ , the number of effective collisions will be  $(n(n-1)/2) n_3$  times (11). Thus in case of the formation of a symmetrical molecule the well-known factor  $\frac{1}{2}$  must be applied to (11). In addition to this, in most cases the reaction can occur only for definite relative orientations of the angular momenta of the atoms and this must be taken care of by another factor giving the probability of such an orientation. It may be pointed out again that (11) is only an upper limit for the rate of association and one could probably somewhat lower it by choosing  $H_0$  more appropriately.

5

Equation (11) gives always an upper limit for the rate of association. However, if  $V - V_0$  can assume negative values, this upper limit can be lowered somewhat quite easily. Indeed, in a system formed by three atoms, the total relative energy  $H_r = H - \mathbf{P}^2/2M$  never can be negative

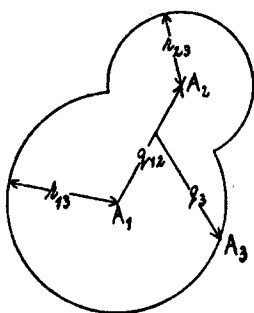


FIG. 1.

and it is not necessary, therefore, to include systems with negative energy into the assembly.

For large distance of the third body, naturally  $H_r > H_0$ . However, at  $\mathbf{p}_3^2/2\mu + V - V_0 = 0$  the  $H_r = 0$  surface cuts the  $H_0 = 0$  surface and goes above it. It is a better choice for  $S$ , then, to use the  $H_r = 0$  surface where it lies above the  $H_0 = 0$  surface, than this one, because no system can go through the  $H_r = 0$  surface,  $H_r$  being (apart from the influence of the walls) an integral of the motion.

The integration of (9) over  $\mathbf{p}_3$  should not be extended, therefore, over the region  $\mathbf{p}_3^2/2\mu + V - V_0 < 0$  in (9) and a factor

$$\int_{\mathbf{p}_3^2 > 2\mu(V_0 - V)} \exp(-\mathbf{p}_3^2/2\mu kT) d\mathbf{p}_3$$

$$\left/ \int_0^\infty \exp(-\mathbf{p}_3^2/2\mu kT) d\mathbf{p}_3 = \right.$$

$$1 - F((V_0 - V)^{1/2}/(kT)^{1/2})$$

$$+ 2((V_0 - V)/\pi kT)^{1/2} e^{-(V_0 - V)/kT} \quad (12)$$

can be inserted to the integrand of (11) wherever  $V_0 - V$  is positive.  $F$  is the error integral

$$F(x) = \frac{2}{\pi^{1/2}} \int_0^x e^{-x^2} dx. \quad (13)$$

Another improvement can be made on (11) if the attractive region of  $V_0$  is preceded by a

repulsive part. However, since it is a rather rare occurrence, it will not be discussed further.

6

If the third body is an inert gas, the total potential energy is the sum of the interactions of the three pairs of atoms.  $V - V_0 = V_{13}(r_{13}) + V_{23}(r_{23})$  is positive in these cases and the correction (12) cannot be applied. The integrand of (11), as function of  $q_3$  has a rather sharp maximum on two spherical portions, represented in Fig. 1. The radius  $r_{13}$  of the sphere around  $A_1$  is the sum  $a_{13}$  of the collision radii of  $A_1$  and  $A_3$ , similarly  $r_{23}$  is the sum  $a_{23}$  of the collision radii of  $A_2$  and  $A_3$ . On the first sphere, one can introduce instead of  $q_3$  polar coordinates around  $A_1$ . Integration over the polar angles gives the solid angle  $\alpha_{13}$  of the first spherical portion. This is

$$\alpha_{13}(q_{12}) = \pi[(a_{13} + q_{12})^2 - a_{23}^2]/a_{13}q_{12} \quad (14a)$$

for  $q_{12} < a_{13} + a_{23}$  and

$$\alpha_{13}(q_{12}) = 4\pi \quad (14b)$$

for  $q_{12} > a_{13} + a_{23}$ . On the sphere around  $A_1$ , one can set  $V - V_0 = V_{13}(r_{13})$ , and the derivative of this, with respect to  $q_{12}$ , at constant  $q_3$ , is  $m_2/(m_1 + m_2)$  times the derivative with respect to  $r_{13}$ . Taking the factor  $a_{13}^2 \alpha_{13}(q_{12})$  out of the integral, one must integrate  $|\partial V_{13}/\partial r_{13}| \exp(-V_{13}/kT)$  with respect to  $r_{13}$  between 0 and  $\infty$ , which gives just  $kT$ . One obtains, performing a similar transformation on the sphere around  $A_2$  also,

$$k = -\frac{(2\pi m, kT)^{-1}}{m_1 + m_2} \int_{V_0 < 0} d\mathbf{q}_{12}$$

$$\cdot V_0 [m_2 a_{13}^2 \alpha_{13}(q_{12}) + m_1 a_{23}^2 \alpha_{23}(q_{12})]$$

$$= -2\pi \left( \frac{2\pi m_r}{kT} \right)^{1/2} \int_{V_0 < 0} V_0 q_{12} \{ (a_{13}^2 - a_{23}^2) \cdot$$

$$\cdot (a_{13}/m_1 - a_{23}/m_2) + 2(a_{13}^2/m_1 + a_{23}^2/m_2) q_{12}$$

$$+ (a_{13}/m_1 + a_{23}/m_2) q_{12}^2 \} dq_{12}. \quad (15)$$

In the last expression, (14a) has been used throughout because in most practical cases  $V_0$  is very small for  $q_{12} > a_{13} + a_{23}$ .

This equation will be compared with the experimental results of Rabinowitch and W. C.

Wood<sup>9</sup> on the recombination of iodine atoms.

For  $V_0$  the Morse curve was used

$$V_0 = D(e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)}) \quad (16)$$

with<sup>10</sup>  $D = 2.46 \cdot 10^{-12}$  erg,  $\alpha = 1.83 \cdot 10^8$  cm<sup>-1</sup>,  $r_0 = 2.66 \cdot 10^{-8}$  cm. This gives

$$-\int V_0 q_{12}^2 dq_{12} = 2.7 \cdot 10^{-35} \text{ erg cm}^3$$

and

$$-\int V_0 q_{12}^3 dq_{12} = 0.91 \cdot 10^{-42} \text{ erg cm}^4.$$

In this case,  $a_{13} = a_{23} = r_J + r_3$  and the values shown in Table I were adopted for the radii.<sup>11</sup> The last line gives the values calculated by (14). These must be divided first by 2, because the associating molecules are identical, and next by 16, because only one of the ten states formed by two  $^2P_{3/2}$  iodine atoms leads to the normal state of the molecule. The experimental results are compared with the calculated ones in Table II.

Although the disagreement is not very great, it is important to notice that the calculated values are lower throughout than the experimental ones. For the molecules  $H_2$ ,  $N_2$ ,  $O_2$  this is, perhaps, not so serious, because (15) should hold for atoms only.<sup>12</sup> For He and A, however, (15) should definitively give an upper limit for the reaction rate. The calculated values should be indeed materially higher than the observed ones.

One possible source of error is contained in the radii of Table I. It would seem, however, that these hardly can be in error by a sufficient amount to explain the discrepancy. The second source of error lies in the potential curve (16). It cannot be expected, of course, that the Morse curve be accurate throughout. In fact, if one determines the  $\alpha$  of (16) from the anharmonicity of the vibration instead of dissociation energy and vibrational frequency,<sup>13</sup> one obtains  $1.47 \cdot 10^8$

cm<sup>-1</sup>. This would compensate the discrepancy. However, the curve of Brown<sup>14</sup> for  $V_0$  integrated directly, gives practically the same result as (16).

It is possible also that not only a  $O_g^+$  state is strongly attractive among the 10 different states

TABLE I.

	He	A	H <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>
$r \cdot 10^8$	1	1.43	1.09	1.58	1.48
$k \cdot 10^{31}$	4.5	6.5	5.4	7	6.7

TABLE II.

	He	A	H <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>
calc. $k \cdot 10^{31}$	0.14	0.20	0.17	0.22	0.21
exp " "	0.18	0.36	0.40	0.66	1.05

arising from two  $^2P_{3/2}$  iodine atoms. Although all states known so far are either repulsive or only very weakly attractive, this possibility must be left open. No such difficulty would come up at the calculation of the rate of recombination of H atoms, e.g., since all states are known in that case.

There is one more point which should be mentioned. For very large  $q_{12}$ , the Morse curve is not valid and the attraction due to the magnetic moment of the spins decreases only as the inverse third power of  $q_{12}$ . Since the square bracket of (15) becomes  $8\pi m_2 a_{13}^2$  for very large  $q_{12}$ , the integral appears to diverge logarithmically. It does not appear sensible, however, to consider two atoms as forming a molecule if, in all probability, they will suffer a dissociating collision before completing a vibration. One is thus led to extending the integration over  $q_{12}$  to the mean free path only. The contribution of the magnetic dipole forces then becomes negligible and the breaking down of (15) (caused by the incorrect situation of  $S$ ) does not become serious.

<sup>9</sup> E. Rabinowitch and W. C. Wood. J. Chem. Phys. 4, 497 (1936).

<sup>10</sup> Cf. for the spectroscopic data, H. Sponer, *Molekülspektren* (Berlin, 1936), Vol. I, p. 18.

<sup>11</sup> Cf. Landolt-Börnstein's Tables, 1st Ergänzungsband, p. 69. The radius of Xe, i.e., 1.75 Å, was used for J.

<sup>12</sup> In addition to this, the formation of an intermediate iodide of the third body may be considered. Cf. reference 9.

<sup>13</sup> For a discussion of this and related questions, cf. reference 10, Vol. 2, p. 103 f.

<sup>14</sup> W. G. Brown, Phys. Rev. 38, 1187 (1931).

<sup>15</sup> Cf. reference 14, also J. H. Van Vleck, Phys. Rev. 40, 544 (1932).