AP The Journal of Chemical Physics

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Citation: J. Chem. Phys. **29**, 294 (1958); doi: 10.1063/1.1744477 View online: http://dx.doi.org/10.1063/1.1744477 View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v29/i2 Published by the AIP Publishing LLC.

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of E_r spanning factors of 15 to 30, with standard deviation in Q that is less than our best estimate of the reliability of measurements of the relative values of mass spectral intensity ratios of the magnitude of those involved in the determination of the reaction cross sections (Q's). There is no systematic variation of the reaction cross section with temperature of the gas in the range 380-600°K, and the reaction cross section decreases with the reduced mass of the isotopic reactant pairs.

As is shown in the accompanying paper, these are the behaviors to be expected for the reactions of charged with uncharged simple particles when the reactions involve no activation energies. Details of the comparison of the theory and experiment are to be found in the companion paper.

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 29, NUMBER 2 AUGUST, 1958

Reactions of Gaseous Molecule Ions with Gaseous Molecules. V. Theory

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(Received November 29, 1957)

Ion-molecule reactions of the sort observed as secondary reactions in mass spectrometers have been treated by the methods of the modern kinetic theory; that is, the rate of reaction is expressed in terms of the velocity distribution functions of the reactants and the cross section for the reaction. The cross section, which is calculated by means of the properties of the classical collision orbits, is found to have an inverse square root dependence on energy. The ion distribution function, which is far from Maxwellian, is found by means of an explicit solution of the Boltzmann equation. A simple relation is given which relates the mass spectrometric data to the specific rate of the same reaction under thermal conditions. For the simpler molecules, this rate may be calculated completely a *priori*, with excellent agreement with experiment.

 \mathbf{I}^{N} a recent communication,¹ it was reported that for a number of reactions of the form

$X^++YH \rightarrow XH^++Y$,

which are observed in mass spectrometers when the ion source pressure is greater than normally used in analytical work, the phenomenological reaction cross sections (defined in references 1 and 2) are inversely proportional to the square root of the ion repeller voltage and of the reduced mass μ of the reactants and are independent of the temperature. In part, these findings are in accord with the theory of such reactions developed by Eyring *et al.*,² that is, the Eyring theory predicts independence of temperature and inverse square root dependence on reduced mass for the reaction rate.

However, the Eyring theory, based as it is on equilibrium statistical mechanics, requires that the reactants possess a Maxwellian distribution in velocity space, while here the ions have been accelerated by the ion repeller field and so are far from Maxwellian.

Field, Franklin, and Lampe³ recently presented a

theory which takes account of the acceleration of the ions, but only approximately, by the methods of the old kinetic theory. The concept of a reaction cross section is introduced, and estimated by a classical analogy with the method of the preceding work. It is recognized that the cross section is a function of energy, but the average is taken as the value at the average energy. Such a procedure, which is characteristic of the old kinetic theory, is adequate for a sharply peaked distribution, but less so for the ionic distribution, which, as will be shown, has a peak whose position is space-dependent. Moreover, a heuristically derived efficiency factor is introduced which as will also be, shown, is unnecessary.

It is the purpose of this communication to present a theory based on the rigorous kinetic theory of gases in terms of the notion of reaction cross section. Such a theory is independent of any assumption of nearequilibrium, but rather is valid for any distribution, and in particular the rather peculiar one of interest. An accompanying paper is devoted to a description of the experimental details.⁴

In general, the rate of reaction p at a point may be expressed in terms of the velocity distributions f_1 , f_2 of the two reactants and of the microscopic cross section σ (defined in the fashion usual in nuclear physics),

¹ D. P. Stevenson and D. O. Schissler, J. Chem. Phys. 23, 1353 (1955). ² Eyring, Hirschfelder, and Taylor, J. Chem. Phys. 4, 479

^{(1936).}

^a Field, Franklin, and Lampe, J. Am. Chem. Soc. 79, 2419 (1957).

⁴ D. P. Stevenson and D. O. Schissler, J. Chem. Phys. 29, 282 (1958).

with result

$$p = \iint [f_1(\mathbf{v}_1)] [f_2(\mathbf{v}_2)] [g\sigma(g)] d\mathbf{v}_1 d\mathbf{v}_2.$$
(1)

Here g is the relative velocity $|\mathbf{v}_1 - \mathbf{v}_2|$.

Of the three factors in the integral above, the ionic distribution function has the least familiar form. Consider the situation in the ion source. The major constituents are neutral molecules at an extremely low pressure. A uniform electric field exists in a direction which we may take as the z axis. At right angles to this is an electron beam localized over a short distance in z. Within the electron beam molecules are ionized, then accelerated by the electric field. Thus the distribution of ions in velocity space is a function of their positions in the ion chamber. It is possible to solve the Boltzmann equation for this function subject to the assumption of zero electron beam thickness.

The neutral molecules, on the other hand, are in thermal equilibrium essentially undisturbed by the small number of electronic collisions, so that their distribution is Maxwellian, and thus presents no difficulty.

The cross sections are found by means of an unusual classical argument, based on the properties of orbits in central force fields. The treatment appears rigorous for a certain class of molecules and leads to the result that the cross section is independent of the specific chemical nature of the reactants, but rather is a function only of such classical parameters as mass, charge, and electric polarizability.

THE DISTRIBUTION FUNCTION

The variation of a molecular distribution function with time and position is given by the Boltzmann equation⁵

$$(\partial f/\partial t) + \mathbf{v} \cdot (\partial f/\partial \mathbf{r}) + (\mathbf{F}/m) \cdot (\partial f/\partial \mathbf{v}) = Q$$
 (2)

where Q is the collisional term. In this problem the gas is so dilute that the only contribution of any consequence to Q is the primary ionization process. The electron beam in the ion chamber is thin and flat and roughly monoenergetic. Let the coordinate system be chosen in such a way that the plane z=0 is within the beam, and let it be assumed that the beam is strictly planar. Furthermore, it is an excellent approximation to take the molecular velocity as unchanged by ionization, since the electron mass is so small that momentum transfer is negligible. Then the number of ions formed, per unit volume, per unit velocity range is

$$B\delta(z)\,(m/2\pi kT)^{3/2}\exp{-mv^2/2kT},$$

where *m* and *v* refer to the ion, $\delta(z)$ is the Dirac delta function, and *B* is the number of ionizations per unit area on the plane.

The ion repeller field is at right angles to the electron beam so that only the z component of the field is not zero. Furthermore, since only the steady state solution is desired, the time derivative term vanishes. The distribution function f then factors into three parts, of which those for v_x and v_y are simply one-dimensional Maxwellian distributions. The z-component equation for $f(v_{z}, z)$,

$$v_{z}(\partial f/\partial z) + (eE/m) (\partial f/\partial v_{z})$$

= B $\delta(z) (m/2kT)^{\frac{1}{2}} \exp(-mv_{z}^{2}/2kT)$ (3)

where E is the field and e the charge of the ion, remains to be solved.

The substitution

$$u = (1/kT) \left(\frac{1}{2}mv_z^2 - eEz \right)$$

leads to the equation

$$z(\partial f/\partial z) = +G\delta(z) \qquad \text{for } v_z \ge 0, \quad (4)$$

$$=-G\delta(z)$$
 for $v_z < 0$, (4')

where

$$G = \frac{B}{\pi^{\frac{1}{2}} 2kT} \frac{m}{u} \qquad \text{for } u > 0$$

for
$$u < 0$$

In terms of z and v_z the solution is

= 0

$$f(v_{z}, z) = \nu(v_{z}, z) \frac{B}{\pi^{\frac{1}{2}}} \frac{m}{2kT} \frac{\exp\left[-(1/kT)\left(\frac{1}{2}mv_{z}^{2} - eEz\right)\right]}{(1/kT)^{\frac{1}{2}}\left(\frac{1}{2}mv_{z}^{2} - eEz\right)}$$
(5)

where ν has a value zero, one or two, as follows

$$\nu = 1 \qquad \text{for } z < 0,$$

= 2
$$\begin{cases} \text{for } z > 0, \\ v_z > 0, \\ \frac{1}{2}mv_z^2 - eEz > 0, \end{cases}$$

= 0
$$\qquad \text{for } v_z < 0,$$

= 0
$$\qquad \text{for } \frac{1}{2}mv_z^2 - eE_z < 0.$$

It is instructive to calculate the flux of ions given by this distribution. For positive z, a simple integration gives the value B independently of the value of z, which means simply that all ions formed eventually reach this region. For negative z the flux is zero. The flux in one definite direction is not zero, but rather has a maximum of B/2 when z=0 and drops very rapidly from that value. As an illustration, the flux is B/20when the dimensionless quantity -Eez/kT is 1.16, and B/200 when it is 1.82. Thus, the number of ions remains appreciable only for a short distance back of the plane of formation.

⁸ Hirschfelder, Curtiss, and Bird, *Molecular Theory of Gases and Liquids* (John Wiley and Sons, Inc., New York, 1949), p. 502.

THE CROSS SECTION

The long-range potential between ions and neutral spherical molecules is of the inverse fourth power sort, that is,

$$\phi(r) = -e^2 \alpha/2r^4, \tag{6}$$

where e is the charge of the ion and α the electric polarizability of the molecule. The orbits of such a potential have been given by Langevin⁶ in connection with a calculation of the mobilities of ions in gases. Typical cases are shown in Fig. 1.

An orbit is determined by two parameters, the relative initial velocity g and the impact parameter b, which is the distance between the initial part of the orbit and a parallel line which goes through the center. For these orbits there is a critical value of b, dependent on g,

$$b_0 = (4e^2 \alpha / \mu g^2)^{\frac{1}{2}},\tag{7}$$

such that orbits for which $b < b_0$ pass through the origin while orbits for which $b \ge b_0$ come no closer than



FIG. 1. A typical family of trajectories as a function of the impact parameter b. The dotted trajectory is the critical one for $b=b_0$ and approaches the circle $r=b_0/\sqrt{2}$. Only trajectories with $b < b_0$ will enter the reaction sphere if it has radius r_c less than this, i.e., $r_c < b_0/\sqrt{2}$. Thus the cross section for entrance into the reaction sphere depends on b_0 but not, within limits, r_c . On the assumption that all molecules which enter the reaction sphere do react, the same may be said of the reaction cross section.

These curves are a modified form of those given by Langevin.⁶

FIG. 2. Dependence of distance of closest approach r_0 upon the impact parameter *b*. The energy enters only through the critical impact parameter b_0 , which is a scale factor.



 $b_0/\sqrt{2}$. The dependence of the distance of closest approach r_0 on b is given in Fig. 2.

Suppose now that there exists a critical radius r_c such that reaction is impossible if the ion-molecule distance be greater than this, and practically certain if less. Then, so long as r_c be between zero and $b_0/\sqrt{2}$, all collisions for which $b < b_0$ must lead to reaction, and so the reaction cross section⁷ is

$$\sigma(g) = \pi b_0^2 = (\pi/g) \left(4e^2 \alpha/\mu \right)^{\frac{1}{2}}.$$
 (8)

Since b_0 varies inversely as the square root of the relative velocity, there must be some collisions at the higher velocities for which it is not true that $r_c < b_0/\sqrt{2}$, but the above expression will still be valid if these are sufficiently few. Thus the polarizability must be large and the mass of the molecule small so that b_0 may be large. Similarly the molecule should be "small," i.e., of limited extent of electron cloud, so that r_c may be small. In addition, energy may be lost to the internal degrees of freedom, so that these are best few and with widely spaced energy levels. Thus the analysis is most likely to be valid for some such reaction as that between a noble gas ion and hydrogen, or hydrogen with hydrogen.⁸

REACTION RATE

The rate of production, per unit volume, of secondary ions is given by Eq. (1), but what is desired is the rate of production integrated over the whole volume. If A be the cross-sectional area of the ion chamber at right angles to the electric field, then this rate is given by

$$P = A \int_{-\infty}^{l} \left(\iint f_1(\mathbf{v}_1) f_2(\mathbf{v}_2) g\sigma(g) d\mathbf{v}_1 d\mathbf{v}_2 \right) dz, \qquad (9)$$

where the lower limit may be taken as minus infinity to excellent approximation, and the upper limit l is the distance from the electron beam to the exit slit. From Eq. (8) it may be seen that the factor, $g\sigma(g)$ in Eq. (9), involving the cross section is independent of g,

⁶ P. Langevin, Ann. chim. phys. 5, 245 (1905).

⁷ Field *et al.* (see reference 3) use the distance of closest approach in place of the impact parameter in calculating the cross section, with result that their value is incorrect by a factor of two.

⁸ It should be recognized that the inverse square root dependence on energy of the cross section is not universal, but rather depends on the particular form of the potential chosen. For an inverse *n*th power potential, $\phi(r) = -\alpha r^{-n}$ (with n>2), the cross section varies as $E^{-2/n}$.

(12)

so the integrations over v_1 and v_2 are independent. Since most of the factors in the integrand are Maxwellian distributions, the integration of these factors may be performed by inspection, leaving

$$P = n_{2}A \left[2\pi e(\alpha/\mu)^{\frac{1}{2}} \right] \left[(B/\pi^{\frac{1}{2}}) \cdot (m_{1}/2kT) \right] \\ \left(\int_{-\infty}^{1} \int_{-\infty}^{\infty} \nu(v_{1z}, z) \frac{\exp[-(1/kT)(\frac{1}{2}m_{1}v_{1z}^{2} - eEz)]}{\left[(1/kT)(\frac{1}{2}m_{1}v_{1z}^{2} - eEz) \right]^{\frac{1}{2}}} \right) dv_{1z} dz,$$
(10)

where n_2 is the number density of the molecules. A change of variable

$$u = (1/kT) \left(\frac{1}{2}m_1 v_{1z}^2 - eEz\right)$$
(11)

and integration with respect to z yields

$$P = n_2 A B(2\pi^{\frac{1}{2}}) e(\alpha/\mu)^{\frac{1}{2}} (2m_1 k T)^{\frac{1}{2}} (l/eEl) F[(eEl/kT)^{\frac{1}{2}}],$$

where if

$$a = (eEl/kT)^{\frac{1}{3}},$$

the function F(a) is given by

$$F(a) = \int_0^\infty (u + a^2)^{\frac{1}{2}} (e^{-u}/u)^{\frac{1}{2}} du.$$
 (13)

Experimental results are given in terms of a quantity Q, the phenomenological cross section, defined by⁴

$$i(S^+) = i(P^+) n_2 l Q,$$
 (14)

where $i(P^+)$ and $i(S^+)$ are the ion currents due to the primary and secondary ions, respectively. Now $i(S^+)$ is proportional to P and $i(P^+)$ to AB, so that

$$Q = (2\pi) \left(2m_1 \alpha e^2 / \mu \right)^{\frac{1}{2}} \cdot (kT/eEl)^{\frac{1}{2}} \cdot F(eEl/kT)^{\frac{1}{2}}.$$
 (15)

The function F(a) is unity when a is zero, but for large a is asymptotically proportional to a, that is,

$$F(a) \sim a\pi^{\frac{1}{2}} \tag{16}$$

Since the potential energy due to the electric field eEl would always be much greater than the thermal energy kT, a would be much greater than unity, and we have

$$Q = 2\pi (2m_1 \alpha e^2/\mu)^{\frac{1}{2}} \cdot 1/(eEl)^{\frac{1}{2}}.$$
 (17)

This cross section, Q, is independent of temperature and varies inversely as the square root of the reduced mass and of the ion repeller voltage.

It is evident from the above that the microscopic cross-section σ and the phenomenological cross-section Q are distinct entities dependent on different variables, and the relation between them is not of a simple form. This distinction is not clear in the previously mentioned paper of Field *et al.*³

It is very important, especially in problems involving radiation chemistry, to be in a position to compare the above cross section with the rate constant for the thermal reaction, that is, for the reaction when the ions as well as the molecules satisfy a Maxwellian distribution. Since $g\sigma(g)$ is a constant, if both f_1 and f_2 are Maxwellian the rate of production of secondary ion (3) is

$$dn_3/dt = n_1 n_2 g\sigma(g) = 2\pi n_1 n_2 (e^2 \alpha/\mu)^{\frac{1}{2}},$$
 (18)

and the rate constant is⁹

$$k = 2\pi (e^2 \alpha / \mu)^{\frac{1}{2}}.$$
 (19)

In terms of Q, k is then given by

$$k = (eEl/2m_1)^{\frac{1}{2}}Q. \tag{20}$$

This equation, it should be noted, has a wider range of validity than either Eq. (17) or Eq. (19). In other words, Eq. (20) would hold approximately so long as $g\sigma(g)$ were nearly constant, even if the value were very different from the theoretical value derived from Eq. (8). Thus, in the cases where the inverse square root law holds for the dependence of cross section on ion repeller voltage, Eq. (20) gives a rigorous interpretation of the mass spectrometric data in terms of ordinarily observable reactions. This is particularly important since many of these reactions are of the sort postulated as intermediate steps in the reactions of radiation chemistry.

One point which remains to be considered is to what extent our conclusions in the foregoing are in error because of the nonzero thickness of the electron beam. It is evident that such a distributed ion source leads to a distribution in the values of z_0 . In order to set an upper limit to the error, let it be assumed that the distribution is uniform for $z_0 \pm 20\%$ and zero beyond. Then the cross section may be calculated by a simple integration, with result that it agrees with the value assuming a plane source at z_0 to within 0.5%. Since the actual distribution is likely to be peaked about z_0 , and has been estimated⁴ to be of lesser extent than assumed above, it would appear that the approximation of zero beam thickness is a good one.

COMPARISON WITH EXPERIMENT

The comparison with the experimental work of Stevenson and Schissler¹ is given in Table I. The first column lists the polarizabilities¹⁰ of the neutral reactants. Those for the various isotopic hydrogens are theoretical and the remaining ones experimental. The second column contains the reduced mass of the reactants in atomic mass units; the third column the ratio of the maximum to the minimum components of the polarizability tensor, and thus gives an estimate of how gross is the error in our assumption of an iso-

⁹ Except for an obvious misprint, Eq. (8c) of reference 2 is the same as Eq. (19). It appears surprising that a classical and quantum mechanical argument should agree exactly, but the Eyring treatment uses a classical approximation at a late stage, so both are really classical.

¹⁰ Hirschfelder et al., reference 5, p. 950.

D.:	1001 1	μ (atomic	amax	k·10 ⁹ m ³ /molecule sec	
Keaction	α.10 ²⁴ cm ³	mass units)	α_{\min}	Expti.	Theoret.
Ar ⁺ +H ₂ →ArH ⁺ +H	0.7894	1.919	1.40	1.68	1.50
$Ar^++HD \rightarrow \begin{cases} AH^++D \\ AD^++H \end{cases}$	0.7829	2.810	1.40	1.43	1.23
$\begin{array}{l} \operatorname{Ar}^{+} + \operatorname{D}_{2} \rightarrow \operatorname{Ar} \operatorname{D}^{+} + \operatorname{D} \\ \operatorname{Kr}^{+} + \operatorname{H}_{2} \rightarrow \operatorname{Kr} \operatorname{H}^{+} + \operatorname{H} \\ \operatorname{Kr}^{+} + \operatorname{D}_{2} \rightarrow \operatorname{Kr} \operatorname{D}^{+} + \operatorname{D} \\ \operatorname{Ne}^{+} + \operatorname{H}_{2} \rightarrow \operatorname{Ne} \operatorname{H}^{+} + \operatorname{H} \\ \operatorname{N}_{2}^{+} + \operatorname{D}_{2} \rightarrow \operatorname{N}_{2} \operatorname{D}^{+} + \operatorname{D} \\ \operatorname{CO}^{+} + \operatorname{D}_{2} \rightarrow \operatorname{COD}^{+} + \operatorname{D} \\ \operatorname{O}_{2} + \operatorname{H}_{2}^{+} \rightarrow \operatorname{O}_{2} \operatorname{H}^{+} + \operatorname{H} \\ \operatorname{O}_{2} + \operatorname{D}_{2}^{+} \rightarrow \operatorname{O}_{2} \operatorname{D}^{+} + \operatorname{D} \\ \operatorname{D}_{2} + \operatorname{D}_{2}^{+} \rightarrow \operatorname{O}_{2} \operatorname{D}^{+} + \operatorname{D} \end{array}$	$\begin{array}{c} 0.7749 \\ 0.7894 \\ 0.7749 \\ 0.7894 \\ 0.7749 \\ 0.7749 \\ 1.60 \\ 1.60 \\ 0.7749 \end{array}$	3.661 1.969 3.845 1.832 3.523 3.523 1.897 3.579 2.015	$ \begin{array}{c} 1.40\\ 1.40\\ 1.40\\ 1.40\\ 1.40\\ 1.40\\ 1.94\\ 1.94\\ 1.40 \end{array} $	1.35 0.487 0.304 0.274 1.72 1.63 7.56 3.56 1.43	1.09 1.47 1.05 1.53 1.10 1.11 2.16 1.52 1.45
$ \begin{array}{l} HCl^{+} + HCl \rightarrow H_{2}Cl^{+} + Cl \\ HBr^{+} + HBr \rightarrow H_{2}Br^{+} + Br \end{array} $	2.63 3.61	17.994 41.001	1.31 1.27	0.43_8 0.22_1	0.89 0.67

TABLE I. Comparison with experimental rate constants.

tropic tensor. Finally, there are the rate constants: the first calculated from the experimental Q's via Eq. (20), and the second the theoretical value of Eq. (19).

As has been shown by Stevenson and Schissler,¹ all of these reactions satisfy the inverse square root law for the dependence of cross section on ion repeller voltage and are temperature independent. Thus the microscopic cross section must have nearly the functional form derived earlier, that is, one varying inversely with the relative velocity, though the constant factors may not be in agreement. For those reactions where the experimentally derived and calculated rate constant are in substantial agreement the inference is that the ioninduced dipole model for the determining stage of the reaction is essentially correct. Of the remaining reactions there are some for which the model is evidently incorrect. Thus, oxygen has a polarizability tensor which is far from isotropic, while hydrogen chloride, hydrogen bromide, and methanol have electric dipole moments.¹¹ There is another group of molecules which has been investigated, that of hydrocarbon ions and molecules^{3,4} for which the phenomenological cross section is a linear function of the reciprocal voltage and for which there is a small temperature dependence. Certainly the functional form of the microscopic cross section in these reactions is not of the sort considered here.

A delicate test of whether the errors are due to some

factor consistently over or underestimated, say a nonunit transmission coefficient or perhaps a polarizability that must be taken as the maximum component of the tensor rather than the mean, lies in the examination of a series of isotopes. Here the ratios of the rate constants should depend only on the variation of the reduced mass and a slight variation of the polarizability. On referring to Table II one sees that the calculated ratios agree with experiment in two cases where the ions are the same, but not in one where the ions are different. This indicates that our view of an ion as a structureless point charge is overly simplified.

CONCLUSIONS

The result of greatest validity in the foregoing work is Eq. (20), the relation between the specific rate of the thermal reaction and the phenomenological cross section, as discussed in the previous section.

Essentially, the mechanism herein proposed is that the course of the reaction depends only on the long range forces between the reactants, as was postulated by Eyring, Hirschfelder, and Taylor.² The limitations of such a view are evident; in the reaction of HD with

TABLE II. Ra	tios of rate	constants for	isotope effect.
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Reaction	k/k' Exptl.	Theoret.
$Ar^++H_2 \rightarrow ArH^++H$	1.24	1.38
$Ar^++HD \rightarrow \begin{cases} ArD^++H\\ ArH^++D \end{cases}$	1.06	1.13
$Ar^++D_2 \rightarrow ArD^++D$	1.00	1.00
$\begin{array}{c} Kr^+ + H_2 \rightarrow KrH^+ + H \\ Kr^+ + D_2 \rightarrow KrD^+ + D \end{array}$	1.60 1.00	1.40 1.00
$\begin{array}{c} Kr^+ + H_2 \rightarrow KrH^+ + H \\ Ne^+ + H_2 \rightarrow NeH^+ + H \end{array}$	1.78 1.00	0.96 1.00

¹¹ In general, one would expect the reaction cross sections for molecules with permanent electric dipole moments, to be greater than those given above, because the net effect would be an attractive force. However, the potential depends on the orientation of the molecule, so that some suitable average potential must be found. If a Boltzmann factor is used, the resulting potential has an inverse fourth power dependence on distance, and so could be included within the model we have assumed. However, the potential as so derived assumes thermal equilibrium, while here, as noted already, we are far from thermal equilibrium. The matter is speculative, and must be considered further.

HD⁺, for example, it can only predict the sum of HD_2^+ and H_2D^+ but not the ratio. Our conclusions then are:

(i) that formation of the activated complex depends only on the long range forces,

(ii) that our method of calculation of the probability of formation is valid if certain conditions are met, to wit: no dipole moment, $r_c \leq b_0/\sqrt{2}$, etc., and

(iii) that while in some cases the activated complex

always goes on to react, so that our expression for the rate constant is very close to the experimental, this need not always be so.

ACKNOWLEDGMENT

One of us (GG) wishes to acknowledge several discussions with Professor Farrington Daniels of the University of Wisconsin which served as precursors to the point of view developed herein.