Let us mention some other related subjects. Instead of electromagnetic waves, we may consider elastic waves in a conductor. These waves result in motions of the positive ions with alternating layers of increased or decreased density. This, in turn, creates an oscillating potential field traveling with the wave, and this field may interact with free electrons in the solid. Such a problem was stated by Parmenter, and our discussion would apply directly to this case. Interaction between elastic waves and free electrons in a metal was also suggested by Bardeen and Fröhlich as a possible explanation of superconductivity. It is hoped that the present discussion will help in clarifying this difficult problem. According to condition (72), the elastic waves able to play a dominant role in the mechanism of superconductivity should be those having a very long mean free path and a long lifetime $\theta$. In this respect, special attention should be given to the waves reduced to their zero-point energy of one-half quantum. These waves have abnormally large $\theta$ values and should play an important role in trapping free electrons and making them insensitive to thermal agitation.

1 For a general discussion of these problems see L. Brillouin, Phys. Rev., 74, 90, 1948.
3 Ibid., eqs. (4), (6), and (13).
5 The result can be seen directly on the determinant $a$, since the change from $\omega p k_0$ to $\omega p k_p$ simply means shifting all rows up by $p$ units, and this does not change the value of the infinite determinant.
7 Ibid., pp. 173–177.

NOTE ON THE SIMPLE COLLISION THEORY OF BIMOLECULAR REACTIONS

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The simple collision theory treats bimolecular reactions by gas-kinetic methods, omitting internal degrees of freedom of the reacting molecules as well as steric effects. Two forms of the simple theory have been proposed, based on different assumptions and leading to different results. In the first theory it is assumed that reaction occurs when the kinetic energy of relative motion $E$ exceeds a specified value $\epsilon^*$; the reaction probability is taken to be one above, and zero below, the threshold energy. The reaction cross-section is discontinuous, since it vanishes below the threshold and is constant and equal to the gas-kinetic cross-section above it. The resulting formula for the number of reactive collisions per unit volume per unit time is

$$N = Z e^{-\epsilon^*/kT} \left( \frac{\epsilon^*}{kT} + 1 \right),$$

(1)
where \( Z \) is the total number of collisions per unit volume per unit time and \( \epsilon^* \) is the threshold or activation energy.

In the second theory a rigid-sphere model is used, and it is assumed that reaction occurs if the translational energy associated with the component of the relative velocity along the line of centers, i.e., the radial kinetic energy, at the instant of closest approach exceeds a specified value. Denoting this "line-of-centers energy at contact" by \( \epsilon \), the reaction probability is taken to be unity for \( \epsilon > \epsilon^* \) and zero for \( \epsilon < \epsilon^* \). The resulting formula is

\[
N = Ze^{-\epsilon^* / kT}.
\]

Since \( \epsilon^* \gg kT \) in practice, e.g., \( \epsilon^*/kT \approx 30 \) for measurements of the hydrogen iodide decomposition, formulas (1) and (2) differ by a significant factor in their predictions of absolute reaction rates. It is found in many cases that formula (2) gives remarkably good agreement with experiment, i.e., the observed reaction rates determine collision diameters which are of reasonable orders of magnitude. Furthermore, the transition-state theory, when applied to the same problem, predicts an absolute reaction rate in agreement with equation (2). Because of the rather artificial nature of the second collision theory, it appears of interest to derive equation (2) by kinetic-theory methods in a somewhat more general fashion, without introducing the "line-of-centers energy at contact." In the derivation which follows, explicit account is taken of the potential energy of interaction and its relation to the activation energy. Also, the probability of reaction or the reaction cross-section is obtained explicitly as a function of the total relative kinetic energy of translation.

We assume a very simple classical model for the formation of the activated complex. When the centers of the collision partners approach to within a distance \( r = D \), it is assumed that the molecules "stick together" to form the complex. If there were no forces between the colliding molecules, the cross-section \( \sigma \) for the formation of the activated complex would be simply \( \pi D^2 \). However, at close distances of approach, the "overlap" forces produce a strong repulsion which is responsible for the activation barrier. Let \( V(r) \) denote the spherically symmetric potential energy of mutual repulsion of the colliding molecules with \( V(\infty) = 0 \). Then \( V(D) \) will represent the activation energy \( \epsilon^* \) for this simple model. The distance between centers at closest approach is determined by the relative velocity \( v \) and the impact parameter \( b \). Those and only those values of \( b \) for which the distance of closest approach would be less than \( D \) lead to formation of the activated complex. A simple calculation, which is independent of the form of \( V(r) \), gives

\[
\sigma(E) = \begin{cases} 
\pi D^2 \left[ 1 - \left( \epsilon^*/E \right) \right], & E > \epsilon^*, \\
0, & E < \epsilon^*, 
\end{cases}
\]

where \( E = \mu v^2 / 2 \) is the complete translational energy of the relative motion, and \( \mu \) is the reduced mass. Equation (3) predicts a hyperbolic rise of the cross-section beyond the threshold with an asymptotic approach to the value \( \pi D^2 \). This is to be contrasted with the step-function

\[
\sigma = \begin{cases} 
\pi D^2, & E > \epsilon^*, \\
0, & E < \epsilon^*, 
\end{cases}
\]
which is assumed in the first collision theory. Since the activated complex may in
some cases decompose into the initial reactants rather than into the products of the
reaction, the cross-section for reaction must be smaller than the activation cross-
section. However, since the two cross-sections will usually differ by a factor of the
order of unity, this factor will be considered to be absorbed in the already uncertain collision diameter $D$, and $\sigma$ will be referred to as the reaction cross-section.

Using the well-known formula for the number of collisions per unit volume per
unit time with the relative translational energy in the interval $E$ to $E + dE$, one
obtains for the number of reactive collisions per cubic centimeter per second in the
same energy interval

$$dN = \frac{2v_1v_2}{(kT)^{3/2}} \cdot \left(\frac{2}{\pi\mu}\right)^{1/2} \cdot \sigma(E) e^{-E/kT} E \ dE,$$

where $v_1$ and $v_2$ denote number densities of molecules of different species. On
inserting $\sigma(E)$ from equation (3) and integrating from $\epsilon^*$ to $\infty$, equation (5) becomes

$$N = 2v_1v_2D^2 \cdot \left(\frac{2\pi kT}{\mu}\right)^{1/2} \cdot e^{-\epsilon^*/kT},$$

$$= Ze^{-\epsilon^*/kT}.$$  

Equations (6) and (2) are identical in form. The second collision theory also gives
the same formula for $dN$ as equation (5) with $\sigma(E)$ inserted from equation (3). The
results are the same because the second theory is a special case of the foregoing in
which the potential energy $V(r)$ is chosen to have the form of a step-function, the
step of height $V(D)$ occurring at $r = D$. The condition that the distance of closest
approach be less than $D$ is equivalent to the condition that the radial kinetic energy
at $r = D$ (i.e., the line-of-centers energy immediately before contact) be greater
than $V(D)$.

It is believed that the model proposed here demonstrates the implausibility of the first
collision theory and provides a more satisfactory basis for the results of the
second collision theory. I am obliged to Dr. O. K. Rice for valuable comment on the
manuscript.

1 R. H. Fowler and E. A. Guggenheim, Statistical Thermodynamics (Cambridge: At the Uni-

2 Glasstone, K. J. Laidler, and H. Eyring, The Theory of Rate Processes (New York: McGraw-