# Variational Theory of Chemical Reaction Rates Applied to Three-Body Recombinations\*

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A "variational" theory, which gives a least upper bound to the rate of a chemical reaction, is presented. The reaction is represented by the motion of a point in phase space across a trial surface dividing the "initial" and "final" chemical states. The trial surface is well defined in regions of phase space where interactions causing reaction are negligible, but is subject to arbitrary variations otherwise. It is shown that a least upper bound to the reaction rate can be obtained by calculating the rate at which representative points cross the "trial" surface and then minimizing this rate with respect to allowed variations of the surface. Explicit calculations of the recombination rate of attracting atoms in the presence of repulsive third bodies are made for a simple trial surface having one adjustable parameter. At low temperatures, the experimental rate constants are quite close to the theoretical bounds; at high temperatures, the experimental data fall away from the bounds in a manner which can be understood in terms of various approximations contained in the theory. Promising methods of improving the agreement between theory and experiment are discussed.

## I. INTRODUCTION

BASIC assumption of kinetic theories of chemical A reaction rates is that transitions between states are induced by collisions. This leads to the concept of a "collision complex" through which reacting systems pass from the initial to the final state.<sup>1</sup> The "collision complex" includes those particle configurations for which the interaction inducing the transition is in some sense appreciable, and except for the case of "square well" interactions, its boundaries can only be loosely defined. Thus, absolute calculations of reaction rates based on a knowledge of the interaction potentials are not possible using kinetic theories, and for this reason they have been severely criticized.

In the present paper, we shall present a method for calculating a rigorous upper bound to the rate of a chemical reaction which is free of this difficulty and provides an explicit connection between the reaction rate and the interaction potentials. The method is based on a variational principal and is similar to an approach outlined by Wigner<sup>2</sup> in 1937. The reaction is represented by the motion of a point in phase space across a trial surface which divides the initial and final states of the system. In regions of phase space where interactions causing reaction are unimportant, the trial surface is uniquely defined by the chemical reaction. In the remaining regions, it is ambiguous and will be assumed arbitrary, except that it must not have any "holes." The division of the phase space into "initial" and "final" states by the trial surface will, of course, not be exact. However, for cases where the volume per particle in a gas is large compared to the interaction volume, this will have a negligible effect on the calculation of the gas properties. Since passage through the trial surface is a necessary condition for reaction, a calculation of the rate at which systems cross it in one direction will yield an upper bound to the reaction rate. The least upper bound is obtained by varying the trial surface to find the minimum crossing rate. It will be shown that for appropriately chosen trial surfaces, it is possible to obtain bounds which lie very close to experimentally observed rates, and thus, the theory offers a promising approach to the problem of understanding reaction rates.

Although we shall apply the method specifically to the three-body recombination reaction, it should be noted that the general principle involved in defining a trial surface, which can be varied to yield a least upper bound to a reaction rate, is applicable to a wide class of both chemical and physical problems.

## **II. MATHEMATICAL DEVELOPMENT**

We are interested in reactions of the type

$$A \rightarrow B$$
 (1)

in which a system of three or more atoms in the initial chemical state A goes over into the final chemical state B. We shall assume that electronic transitions do not occur during the reaction and that the motion of the nuclei may be treated classically. With these approximations, the state of the system can be specified by a point in the phase space of the nuclei. Let S be a surface in this phase space which divides the "initial" state A from the "final" state B. In regions where interactions causing reaction are negligible, S is defined by the requirement that it coincide with the surface used to calculate the equilibrium constant for the reaction. In the remaining regions, S is ambiguous and, for practical purposes, arbitrary. In these regions, Scan be chosen to suit our convenience, and any particular choice of S can be regarded as a trial surface subject to arbitrary variations. As usual, such variations will be made by the adjustment of a set of arbitrary parameters  $\alpha_i$  on which S depends.

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<sup>&</sup>lt;sup>1</sup> J. C. Keck, J. Chem. Phys. **29**, 410 (1958). <sup>2</sup> E. P. Wigner, J. Chem. Phys. **5**, 720 (1937).

Since the crossing of S is a necessary condition for reaction, an upper bound to the rate of reaction (1) can be obtained by calculating the rate  $R(\alpha_j)$  at which representative points in phase space flow across S in one direction.  $R(\alpha_j)$  can be expressed as an integral over S of the product of the phase space density  $\rho$ and the normal component of the generalized velocity of representative points. Thus,

$$R(\alpha_j) = \int_{\mathbf{v} \cdot \mathbf{n} > 0}^{S} \mathbf{v} \cdot \mathbf{n} \rho d\sigma, \qquad (2)$$

where  $d\sigma$  is an element of the surface S, **n** is the unit normal to  $d\sigma$ , and **v** is the generalized velocity of a representative point.

In general, one will not be able to specify the density exactly at points in phase space where three-body interactions are important. However, as a consequence of Liouville's theorem, we know that, for regions connected by trajectories satisfying the known conservation laws, the density where interactions are important cannot exceed the maximum density  $\rho_m$  where interactions are unimportant. Thus, we will still obtain an upper bound to the reaction rate if we substitute  $\rho_m$  for  $\rho$  in Eq. (2):

$$R_m(\alpha_j) = \int_{\mathbf{v} \cdot \mathbf{n} > 0}^{S} \mathbf{v} \cdot \mathbf{n} \rho_m d\sigma, \qquad (3)$$

Equation (3) may be transformed into an expression more convenient for calculation as follows: We define S by means of the equation,

$$\boldsymbol{\phi}(\boldsymbol{p}_i, \boldsymbol{q}_i, \boldsymbol{\alpha}_j) = 0. \tag{4}$$

In terms of  $\phi$  the unit normal to S may be written,

$$\mathbf{n} = \nabla \phi / | \nabla \phi |. \tag{5}$$

By substituting Eq. (5) into Eq. (3) and expanding the dot product gives

$$R_m(\alpha_j) = \sum_i \int \rho_m \left( \dot{p}_i \frac{\partial \phi}{\partial p_i} + \dot{q}_i \frac{\partial \phi}{\partial q_i} \right) \frac{d\sigma}{|\nabla \phi|}.$$
 (6)

Substituting Hamilton's equation of motion into Eq. (6) gives

$$R_{m}(\alpha_{j}) = \sum_{i} \int \rho_{m} \left( -\frac{\partial H}{\partial q_{i}} \frac{\partial \phi}{\partial p_{i}} + \frac{\partial H}{\partial p_{i}} \frac{\partial \phi}{\partial q_{i}} \right) \frac{d\sigma}{|\nabla \phi|}.$$
 (7)

The quantity in parenthesis is the Jacobian  $J_i$  of the transformation from  $dHd\phi$  to  $dp_i dq_i$ . Thus, Eq. (7) may be rewritten,

$$R_m(\alpha_j) = \sum_i s_i \int \rho_m \frac{dH d\phi d\sigma}{dp_i dq_i \mid \nabla \phi \mid},$$
 (8)

where

$$s_{i} = \begin{cases} J_{i} / |J_{i}|, & J_{i} \neq 0 \\ 0, & J_{i} = 0. \end{cases}$$
(9)

Since  $d\phi/|\nabla\phi|$  is the element of length perpendicular to  $d\sigma$ , the factor  $d\sigma d\phi/|\nabla\phi|$  is just the volume element in phase space  $\prod dp_i dq_i$ , and Eq. (8) may be rewritten,

$$R_m(\alpha_j) = \sum_i s_i \int \rho_m dH \prod_{k \neq i} dp_k dq_k.$$
(10)

The integration of Eq. (10) is to be performed subject to the constraints  $\phi = 0$  and  $\mathbf{v} \cdot \mathbf{n} = \sum_{i} J_i \ge 0$ . Having obtained the value of  $R_m(\alpha_i)$  from Eq.

Having obtained the value of  $R_m(\alpha_j)$  from Eq. (10), we may find the values of  $\alpha_j$ , for which it is a minimum by setting

$$\partial R_m(\alpha_j) / \partial \alpha_l = 0. \tag{11}$$

Substitution of the values of the  $\alpha_j$  obtained from Eq. (11) into Eq. (10) gives the least upper bound to the true reaction rate which can be obtained for the assumed "trial" surface and the given interaction potential.

We should like to reiterate the reasons  $R_m(\alpha_i)$  is an overestimate of the reaction rate, because it is important to keep them in mind in comparing theory and experiment. First, we have included in our calculation all crossings of S in one direction, and some of these will be due to single trajectories which cross S more than once. Second, we have extended our integral over all of S and may have included regions which are inaccessible to trajectories originating outside the interaction zone. Finally, we have replaced the true density of points on S by the maximum value it can have consistent with the conservation laws.

In concluding this discussion, we should like to point out that for the special case of a gas in thermodynamic equilibrium

$$\rho_m = \rho_e = \rho_0 \exp(-H/kT). \qquad (12)$$

In Eq. (12) H is the total energy of a three-particle system which is, of course, conserved along a trajectory, and  $\rho_0$  is a constant.

#### III. THREE-BODY RECOMBINATION

To illustrate the application of the foregoing principles, we shall calculate a least upper bound to the equilibrium recombination rate constant for the reaction

$$A_1 + A_2 + A_3 \longrightarrow A_1 A_2 + A_3. \tag{13}$$

For simplicity, we shall assume that  $A_3$  is a repulsive catalyst so that no other reactions are possible. The trial surface S we shall use in this calculation is shown in Fig. 1. It is one of the simplest that can be constructed which includes the effect of the rotational barrier. It depends on a single arbitrary parameter ain terms of which it may be decomposed into two faces  $S^A$  and  $S^B$ . (14)

The face  $S^{A}$  is defined by the relations,

where

$$H_{12} = p_{12}^2 / 2\mu_{12} + l_{12}^2 / 2\mu_{12}r_{12}^2 + V_{12}$$
(15)

is the internal energy of  $A_1A_2$ ,

 $r_3 = a$ :

$$B = V_{12}(z) + \frac{1}{2}z \frac{dV_{12}}{dr_{12}} \bigg|_{z}$$
(16)

 $r_{12} < z$ ,

is the energy of the rotational maximum in the effective potential,  $V_{12}+l_{12}^2/2\mu_{12}r_{12}^2$ , and z is the position of the rotational maximum defined by the condition,

 $H_{12} \leq B$ :

$$(\partial/\partial r_{12}) [V_{12} + l_{12}^2/(2\mu_{12}r_{12}^2)] |_{z} = (dV/dr_{12}) |_{z} - (l_{12}^2/\mu_{12}z^3) = 0.$$
 (17)

In the above equations,  $r_3$  is the separation of  $A_3$  and the center-of-mass of  $A_1$  and  $A_2$ ,  $r_{12}$  is the separation of  $A_1$  and  $A_2$ ,  $p_{12}$  is the radial momentum of  $A_1A_2$ ,  $l_{12}$  is the angular momentum of  $A_1A_2$ ,  $V_{12}$  is the potential energy of  $A_1A_2$ , which is assumed to depend only on  $r_{12}$ , and  $\mu_{12} = m_1m_2/(m_1+m_2)$  is the reduced mass of  $A_1A_2$ . The rate at which representative points in phase space flow across  $S^A$  is simply the rate of binary collisions between molecules  $A_1A_2$  and third bodies  $A_3$  for a collision diameter a. In the present problem, we shall be interested in the rate of binary collisions in which the energy to dissociate  $A_1A_2$  is available in the center-of-mass system of  $A_1A_2+A_3$ . This rate will be called the "available energy" collision rate.

The face  $S^{\mathbf{B}}$  is defined by the relations,

$$H_{12} = B: \quad r_3 \ge a: \quad r_{12} \le z.$$
 (18)

The rate at which representative points in phase space flow across  $S^{B}$  is the analog of the Wigner rate, including the effect of the rotational barrier, and will be called the barrier rate.

It should be clear from Fig. 1 and the definitions of  $S^{A}$  and  $S^{B}$  that S satisfies the requirements for an acceptable trial surface. The total rate of flow of representative points across S is just the sum of the available





F1G. 2. Part (a) shows angular coordinates used in the present calculation. Part (b) shows coordinates giving the relative positions of the three atoms  $A_1$ ,  $A_2$ , and  $A_3$ .

energy and barrier rates and is a function of the parameter a. The minimum value of this sum with respect to variations of a will be called the variational rate.

## **Available Energy Rate**

The equilibrium rate constant

$$k^{\mathbf{A}}(a) = R_m^{\mathbf{A}}(a) / [\mathbf{A}_1] [\mathbf{A}_2] [\mathbf{A}_3]$$

corresponding to the available energy rate can be obtained by combining Eqs. (10) and (12) and eliminating the center-of-mass coordinates. The result is

$$k^{A}(a) = (g_{12}/Z_{f}) \int \exp(-E/kT)$$
$$\times dEdl_{3}d\omega_{3}dm_{3}d\phi_{3}dp_{12}dr_{12}dl_{12}d\omega_{12}dm_{12}d\phi_{12}, \quad (19)$$

where  $g_{12}$  is the electronic degeneracy associated with the potential  $V_{12}$ ,

$$Z_f = g_1 g_2 (2\pi \mu_{12} k T)^{\frac{3}{2}} (2\pi \mu_3 k T)^{\frac{3}{2}}$$
(20)

is the partition function for  $A_1+A_2+A_3$  in the centerof-mass system,  $g_1$  and  $g_2$  are the electronic degeneracies of  $A_1$  and  $A_2$ , respectively,

$$E = (p_{12}^2/2\mu_{12}) + (l_{12}^2/(2\mu_{12}r_{12}^2) + (p_3^2/2\mu_3) + (l_3^2/2\mu_3r_3^2) + V \quad (21)$$

is the total energy of  $A_1+A_2+A_3$  in the center-of-mass system,  $p_3$  is the radial momentum of  $A_3$  with respect



FIG. 3. Schematic diagram showing limits of integration for Eq. (22).

to  $A_1A_2$ ,  $l_3$  is the angular momentum of  $A_3$  about  $A_1A_2$ ,  $\mu_3 = (m_1+m_2)m_3/(m_1+m_2+m_3)$  is the reduced mass of  $A_3$  and  $A_1A_2$ , and V is the total potential energy of  $A_1+A_2+A_3$ , which we assume depends only on the relative positions of the three particles. The remaining coordinates are defined in Fig. 2.

The integral in Eq. (19) is to be taken over the surface  $S^{A}$  defined by Eq. (14), subject to the conditions  $E \ge 0$  imposed by the requirement that the energy for dissociation be available, and  $E - V \ge p_{12}^2/2\mu_{12} + l_{12}^2/2\mu_{12}r_{12}^2 + l_{3}^2/2\mu_{3}r_{3}^2$ , imposed by the requirement that the radial kinetic energy of  $A_3$  with respect to  $A_1A_2$  must be positive. The requirement that only representative points crossing  $S^{A}$  in one direction be included has been satisfied in Eq. (19) by taking the factor s defined by Eq. (9) equal to +1.

In order to evaluate Eq. (19), it is convenient to introduce the angles  $\alpha_1$  and  $\beta_3$  shown in Fig. 2 in place of  $m_{12}$  and  $\phi_{12}$ . This transformation, for which the Jacobian is simply  $l_{12} \sin \alpha_1$ , enables us to express the total potential energy V in terms of  $r_{12}$ ,  $r_3$ , and  $\alpha_1$ . The integration with respect to  $dEdl_3 dm_3 d\phi_3 d\omega_{12} d\beta_3$ may then be carried out in a straightforward manner and gives

$$k^{A}(a) = (g_{12}/g_{1}g_{2}) 4\pi a^{2} (2kT/\mu_{3})^{\frac{1}{2}} \int (I_{1}+I_{2}) r_{12}^{2} dr_{12} d\cos\alpha_{1},$$
(22)

where

$$I_1 = \int [1 - (x^2 + y + u)] dx dy, \quad 0 < x^2 + y < -u, \quad (23a)$$

and

$$I_{2} = \int \exp[-(x^{2} + y + u)] dx dy,$$
$$-u < x^{2} + y < b - u_{12}. \quad (23b)$$

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In the foregoing equations,

$$u = V/kT,$$
  

$$u_{12} = V_{12}/kT,$$
  

$$b = B/kT,$$
  

$$x = p_{12}/(2\mu_{12}kT)^{\frac{1}{2}},$$
  

$$y = l_{12}^{2}/2\mu_{12}kTr_{12}^{2}.$$

The integration of Eq. (23a) is elementary and gives

$$I_{1} = \begin{cases} 2\left[\frac{4}{15}(-u)^{5/2} + \frac{2}{3}(-u)^{\frac{3}{2}}\right], & u < 0\\ 0, & u > 0. \end{cases}$$
(24)

The integration of Eq. (23b) involves transcendental functions and is quite complicated. Fortunately, it has been found numerically that in all practical cases the contribution to the final result arising from  $I_2$  is smaller than that from  $I_1$ , and, therefore, to a first approximation we can neglect  $I_2$ .

We can now integrate Eq. (22) approximately with respect to  $d \cos \alpha_1$ . To do this, we divide the range of integration into two parts, in which  $u \leq 0$  and  $u \geq 0$  as shown schematically in Fig. 3. We then assume that the interaction with A<sub>3</sub> varies sufficiently rapidly as a function of  $\alpha_1$  so that it will be a reasonable approximation to set  $u = u_{12}$  over the entire range where  $u \leq 0$ . As a result of this approximation, we obtain

$$k^{A}(a) = (g_{12}/g_{1}g_{2}) 8\pi a^{2} (2kT/\mu_{3})^{\frac{1}{2}} \int_{u_{12} < 0} [\frac{4}{15}(-u_{12})^{5/2} + \frac{2}{3}(-u_{12})^{\frac{1}{2}}](\cos\alpha_{1-} - \cos\alpha_{1+})r_{12}^{2}dr_{12}. \quad (25)$$

To perform the remaining integration over  $dr_{12}$ , we first observe that the integrand in Eq. (25) has a strong maximum in the vicinity of the radius  $r_e$ , where  $u_{12}$  has its minimum. Thus, as a first approximation we can expand the potential  $u_{12}$  about  $r_e$  in a Taylor series

$$u_{12} \approx -D_{12} [1 - \beta_{12}^2 (r_{12} - r_e)^2] / kT, \qquad (26)$$

and evaluate the relatively slowly varying term  $(\cos\alpha_{1-} - \cos\alpha_{1+})r_{12}^2$  at  $r_e$ . The remaining integration then gives

$$k^{A}(a) = (g_{12}/g_{1}g_{2}) 4\pi^{2}a^{2}r_{e}^{2}\beta_{12}^{-1}(\cos\alpha_{1-}-\cos\alpha_{1+})r_{e}$$

$$\times (2D_{12}/\mu_{3})^{\frac{1}{2}}\sum_{n=2}^{3}(1/n!) (D_{12}/kT)^{n-1}, \quad (27)$$

where the angles  $\alpha_{1-}$  and  $\alpha_{1+}$  are defined in Fig. 3. This is the final form of our result. It is identical with the ordinary expression for the available energy rate<sup>3</sup> except for the factor  $(\cos\alpha_{1-}-\cos\alpha_{1+})_{r_e}$ , which accounts for the fact that particles are excluded from regions where the potential is strongly repulsive, and the omission in the summation of the terms n=0 and 1, which result from extending integrations over  $p_{12}$  and  $l_{12}$  to infinity rather than cutting them off at the dissociation limit as we have done.

The approximations made in obtaining  $k^{A}(a)$  are expected to be quite good from a physical standpoint, and it is believed that no serious errors result from their use. Note that a weak van der Waals attraction will not affect our result in the high temperature range where it will subsequently be used.

<sup>&</sup>lt;sup>3</sup> R. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, Cambridge, England, 1939), Chapter XII.

#### **Barrier** Rate

The equilibrium rate constant

$$k^{\mathbf{B}}(a) = R_m^{\mathbf{B}}(a) / [A_1] [A_2] [A_3]$$

corresponding to the barrier rate can be obtained by combining Eqs. (10) and (12) and eliminating the center-of-mass coordinates. The result may be expressed in the form,

$$k^{\mathbf{B}}(a) = (g_{12}/Z_f) \int \exp(-E/kT) dE(s_p dl_{12} d\omega_{12} + s_l dp_{12} dr_{12})$$

$$\times dm_{12} d\phi_{12} dp_3 dr_3 dl_3 d\omega_3 dm_3 d\phi_3, \quad (28)$$

where  $s_p = \pm 1$  and  $s_l = (\partial V / \partial \omega_{12}) / |\partial V / \partial \omega_{12}|$ . The integrations are to be carried out over the surface  $S^{\text{B}}$  defined by Eq. (18) subject to the restriction,

$$s_{p} | \partial (V - V_{12}) / \partial r_{12} | + s_{l} | \partial V / \partial \omega_{12} | \cdot | \partial p_{12} / \partial l_{12} | \ge 0$$
(29)

imposed by the requirement that only representative points crossing  $S^{B}$  in one direction be counted.

Note that the first and second terms in Eq. (28) give, respectively, the contribution to  $k^{B}(a)$  due to vibrational and rotational transitions.

To integrate Eq. (28) it is convenient to replace  $dEd\omega_{12}dm_{12}d\phi_{12}$  in the vibrational term by  $dr_{12}d\alpha_{1}d\beta_{3}d\beta_{12}$ and  $dEdp_{12}dm_{12}d\phi_{12}$  in the rotational term by  $dl_{12}d\alpha_{1}d\beta_{3}d\beta_{12}$ . These transformations, for which the Jacobians are, respectively,  $[\partial (V-V_{12})/\partial r_{12}]l_{12} \sin\alpha_{1}$ and  $[\partial (V-V_{12})/\partial \alpha_{1}](\partial p_{12}/\partial l_{12})l_{12} \sin\alpha_{1} \cos\beta_{12}$ , permit the integration over  $d\beta_{3}d\beta_{12}dp_{3}dl_{3}d\omega_{3}dm_{3}d\phi_{3}$  to be carried out. The result is

$$k^{B}(a) = (g_{12}/g_{1}g_{2}) 4\pi (8kT/\pi u_{12})^{\frac{1}{2}} \int \exp[-(b+u-u_{12})]$$
  
×[|  $\partial(u-u_{12})/\partial r_{12} | r_{12}\eta_{1} + | \partial(u-u_{12})/\partial \alpha_{1} | \gamma \cos\eta_{1}]$   
× $r_{3}^{2}dr_{3}r_{12}dr_{12}dr_{2}dvd \cos\alpha_{1}, (30)$ 

where

$$\eta_1 = \begin{cases} \pi/2, & \gamma^2 \tan^2 \theta_1 \leq 1 \\ \tan^{-1} (\gamma^2 \tan^2 \theta_1 - 1)^{-\frac{1}{2}}, & \gamma^2 \tan^2 \theta_1 \geq 1, \end{cases}$$

and

$$\gamma = r_{12} \mid \partial p_{12} / \partial l_{12} \mid.$$

As before, u = V/kT,  $u_{12} = V_{12}/kT$ , b = B/kT,  $y = l_{12}^2/2\mu_{12}kTr_{12}^2$ . The angle  $\theta_1$  is shown in Fig. 2(b).

It is interesting to note that Eq. (30) shows that if the total potential V is spherically symmetric about the center-of-mass of  $A_1A_2$  (i.e., independent of  $\alpha_1$ ), then the contribution to the reaction rate from rotational transitions is identically zero.

To proceed further, we must specify the potentials  $V_{12}$  and V. Two-body potentials have been determined for many molecules from spectroscopic measurements and scattering experiments and we can assume  $V_{12}$  is known. Three-body potentials are virtually nonexistent, however, and we cannot specify V with any degree of

confidence at all. About the best that can be done is to approximate V as the sum of the two-body potentials,  $V_{12}(r_{12})$ ,  $V_{13}(r_{13})$ , and  $V_{23}(r_{23})$ , where  $V_{13}$  and  $V_{23}$ represent the interactions of the third body with each of the recombining atoms. If  $V_{13}$  and  $V_{23}$  are sufficiently short range, then the region of configuration space in which they are simultaneously important is small, and we can separate  $k^{\text{B}}(a)$  into two parts,  $k_1^{\text{B}}(a)$  and  $k_2^{\text{B}}(a)$ , corresponding, respectively, to configurations in which  $|V_{13}| \ge |V_{23}|$  and  $|V_{23}| \ge |V_{13}|$ . Roughly speaking  $k_1^{\text{B}}(a)$  may be thought of as the contribution to  $k^{\text{B}}(a)$  from collisions of A<sub>3</sub> with A<sub>1</sub> and  $k_2^{\text{B}}(a)$  as the contribution from collision of A<sub>3</sub> with A<sub>2</sub>. With these approximations, we can write  $k_1^{\text{B}}(a)$  in the form,

$$k_{1}^{B}(a) = (g_{12}/g_{1}g_{2}) 4\pi (8kT/\pi\mu_{12})^{\frac{1}{2}} \cdot [m_{2}/(m_{1}+m_{2})] \int \exp[-(b+u_{13})] \times |du_{13}/dr_{13}| (\eta_{1}\cos\theta_{1}+\gamma\cos\eta_{1}\sin\theta_{1}) \times r_{13}^{2}dr_{13}r_{12}^{2}dr_{12}dyd\cos\theta_{1}, \quad (31)$$

where the integral is to be extended over the region  $|V_{13}| \ge |V_{23}|$ . Note that we have eliminated  $r_3$  and  $\alpha_1$  in favor of  $r_{13}$  and  $\theta_1$ .

The corresponding expression for  $k_{2^{B}}$  can be obtained from Eq. (31) by simply interchanging the subscripts 1 and 2.

The integration over  $d \cos\theta_1$  may now be performed and gives

$$k_{1}^{\mathrm{B}}(a) = (g_{12}/g_{1}g_{2})\pi^{2}(8kT/\pi\mu_{12})^{\frac{1}{2}}$$

$$\times [m_{2}/(m_{1}+m_{2})]\int \exp[-(b+u_{13})] |du_{13}/dr_{13}|$$

$$\times (f_{p}+\gamma^{2}f_{l})(1+\gamma^{2})^{-\frac{1}{2}}r_{13}^{2}dr_{13}r_{12}^{2}dr_{12}dy, \quad (32)$$

where

$$f_{p} = \begin{cases} 1 - \frac{\tan\theta_{1m}}{|\tan\theta_{1m}|} (2/\pi) \{ \tan^{-1} [(1+\gamma^{2})^{\frac{1}{2}} \tan\eta_{1m}] \\ - (1+\gamma^{2})^{\frac{1}{2}} \eta_{1m} \sin^{2}\theta_{1m} \}, & \gamma^{2} \tan^{2}\theta_{1m} \ge 1 \\ 1 - \frac{\tan\theta_{1m}}{|\tan\theta_{1m}|} [1 - (1+\gamma^{2})^{\frac{1}{2}} \sin^{2}\theta_{1m}], & \gamma^{2} \tan^{2}\theta_{1m} \le 1 \end{cases}$$

$$(33a)$$

and

$$f_{l} = \begin{cases} 1 - \frac{\tan\theta_{1m}}{|\tan\theta_{1m}|} (2/\pi) \left\{ \tan^{-1} \left[ (1+\gamma^{2})^{\frac{1}{2}} \tan\eta_{1m} \right] \right. \\ \left. + \frac{(1+\gamma^{2})^{\frac{1}{2}}}{\gamma^{2}} \frac{\cos^{2}\theta_{1m}}{\tan\eta_{1m}} \right\}, \qquad \gamma^{2} \tan^{2}\theta_{1m} \ge 1 \\ \left. 1 - \frac{\tan\theta_{1m}}{|\tan\theta_{1m}|}, \qquad \gamma^{2} \tan^{2}\theta_{1m} \le 1. \end{cases}$$
(33b)



FIG. 4. Schematic diagram showing limits of integration for Eq. (31). The primed and unprimed quantities refer to the two cases given in Eq. (34).

The angle  $\theta_{1m}$  is defined by the relations,

$$\theta_{1m} = \begin{cases} [(r_3^2 - r_1^2 - r_{13}^2)/2r_1r_{13}]_{V_{13} = V_{23}}, \\ (r_3)_{V_{13} = V_{23}} \ge a \\ [(a^2 - r_1^2 - r_{13}^2)/2r_1r_{13}]_{V_{13} = V_{23}}, \\ (r_3)_{V_{13} = V_{23}} \le a. \end{cases}$$
(34)

and is shown in Fig. 4 for the two cases indicated.

The functions  $f_p$  and  $f_l$  are essentially the effective solid angles over which  $A_3$  induces vibrational and rotational transitions. They are roughly of the form  $(1-\cos\theta_{1m})$  and are shown in Fig. 5 as a function of  $\theta_{1m}$  for several values of  $\gamma^2$ . As one might expect the derivative of  $f_p$  with respect to  $\theta_{1m}$  has maxima in the neighborhood of 45° and 135°, indicating that vibrational transitions are most important at these angles,



FIG. 5. Curves showing the function  $f_p$  and  $f_l$  defined by Eqs. (33a) and (33b).

while the derivative of  $f_l$  has a maximum at 90°, indicating that rotational transitions are most important at this angle. Also note that for all values of  $\gamma^2$ , except infinity, there are finite regions in which  $f_l$  has zero derivative, indicating that rotational transitions are forbidden.

We now assume that the potential  $V_{13}$  has the form shown in Fig. 6(a), i.e., it is strongly repulsive for small separations and has a weak van der Waals attraction at larger separations. The factor  $|du_{13}/dr_{13}|$  $\exp(-u_{13})$  will thus have the form shown in Fig. 6(b). Note that there are two strong maxima at separations  $\alpha_{1+}$  and  $\alpha_{1-}$  defined by the condition,

$$(d/dr_{13})[| du_{13}/dr_{13} | \exp(-u_{13})]_{\alpha_1\pm} = 0 \qquad (35)$$



FIG. 6. Part (a) shows the form of the interaction potential  $V_{13}$ . Part (b) shows the maxima in the function  $|du_{13}/dr_{13}| \exp(-u_{13})$ .

and separated by a zero at  $\sigma_m$  where  $u_{13}$  has its minimum. The integration over  $r_{13}$  can thus be divided into two parts  $0 \le r_{13} \le \sigma_m$  and  $\sigma_m \le r_{13} \le \infty$ . Since the factor  $(f_p + \gamma^2 f_l) r_{13}^2$  varies relatively slowly we may evaluate it  $a_{1-}$  in the part  $0 \le r_{13} \le \sigma_m$  and  $\alpha_{1+}$  in the part  $\sigma_m \le r_{13} \le \infty$  and factor the integrand. The remaining integration is elementary and gives

$$k_{1}^{\mathbf{B}}(a) = (g_{12}/g_{1}g_{2})\pi^{2}(8kT/\pi\mu_{12})^{\frac{1}{2}}[m_{2}/(m_{1}+m_{2})] \times \{a_{1-}^{2}I_{1-}\exp(\epsilon/kT) + a_{1+}^{2}I_{1+}[\exp(\epsilon/kT) - 1]\}, (36)$$

where

$$I_{1\pm} = \int e^{-b} (f_p + \gamma^2 f_l)_{\alpha_1 \pm} (1 + \gamma^2)^{-\frac{1}{2}} r_{12}^2 dr_{12} dy.$$
(37)

Note that in performing the  $r_{13}$  integration above we have assumed there is an equilibrium population of  $A_1A_3$  bound by the van der Waals potential. This implies that the rate-limiting step in the chain

$$A_1 + A_3 + X \longrightarrow A_1 A_3 + X$$
$$A_2 + A_1 A_3 \longrightarrow A_2 A_1 + A_3$$

is the latter reaction. This is almost certainly true when  $\epsilon/kT \lesssim 1$ .

At this point, we may check our results against those obtained by Wigner for the case where the surface separating free and bound states was taken as  $H_{12}=0$ . To do this, we simply set b=0 and neglect the van der Waals attraction, i.e., set  $\epsilon=0$ . The integration over dy may then be carried out and gives

$$k_{1}^{w} = (g_{12}/g_{1}g_{2}) \left[ 8\pi^{2}a_{1-}^{2}/(2\pi\mu_{12}kT)^{\frac{1}{2}} \right]$$

$$\times \left[ m_{2}/(m_{1}+m_{2}) \right] \int_{V_{12}<0} |V_{12}| (1-\cos\theta_{1m})r_{12}^{2}dr_{12}. \quad (38)$$

By adding to this the corresponding expression for  $k_2^w$ , we obtain the Wigner result,

$$k^{w} = (g_{12}/g_{1}g_{2}) 4\pi a_{1-}{}^{2} (2\pi\mu_{12}/kT)^{\frac{1}{2}} \int_{V_{12}<0} |V_{12}| \times [(1/m_{1}) (1-\cos\theta_{1m}) + (1/m_{2}) (1-\cos\theta_{2m})] r_{12}{}^{2} dr_{12}.$$
(39)

In the present calculation, we wish to include the effects of the rotational barrier explicitly. To do this, we carry out an approximate integration with respect to dy using a technique previously employed in the integration of Eq. (32). We first make a change of variables introducing the position of the rotational barrier, z, in place of y. Equation (37) can then be written

$$I_{1\pm} = \int_{z_m}^{\infty} e^{-b} |db/dz| [F_p^{1\pm}(z) + F_l^{1\pm}(z)](z-z_1) z^2 dz,$$
(40)

where

$$F_{p^{1\pm}}(z) = (z - z_{1})^{-1} \int_{z_{1}}^{z} (f_{p})_{a_{1\pm}} (1 + \gamma^{2})^{-\frac{1}{2}} dr_{12} \quad (41a)$$

and

$$F_l^{1\pm}(z) = (z - z_1)^{-1} \int_{z_1}^{z} \gamma^2 (f_l)_{a_1\pm} (1 + \gamma^2)^{-\frac{1}{2}} dr_{12}.$$
 (41b)

The range of integration for Eq. (40) is defined by the requirement that a rotational barrier exist. For many potentials, this is only true if the angular momentum  $l_{12}$  is less than some maximum value  $l_m$ . If  $z_m$  is the position of the rotational barrier corresponding to  $l_m$ ,  $l_{12} \leq l_m$  implies  $z \geq z_m$ . The range of integration for Eqs. (41a) and (41b) is defined by the requirement that the effective potential at  $r_{12}$  must be less than the barrier height, so that the radial momentum  $p_{12}$  will be real. Thus,  $z_1$  is defined as a function of z by the equation

$$u_{12}(z_1) + (z^3/2z_1^2) (du_{12}/dr_{12})|_{s} = u_{12}(z) + \frac{1}{2}z(du_{12}/dr_{12})|_{s}.$$
(42)

We now make the assumption that b increases strongly with decreasing z, so that the factor  $|db/dz| \exp(-b)$  in the integrand has a sharp maximum at a radius  $z_2$  defined by the condition,

$$(d/dz) [| db/dz | \exp(-b) ]_{z_2} = 0, \qquad (43)$$

while the remainder of the integrand varies sufficiently slowly so that it may be approximated by its value at  $z_2$ . The integral may then be factored and integrated with respect to dz. The result is

$$I_{1\pm} = [F_p^{1\pm}(z_2) + F_l^{1\pm}(z_2)](z_2 - z_1)z_2^2 \\ \times [1 - \exp(-B_m/kT)], \quad (44)$$

where  $B_m$  is the maximum value of B and corresponds to  $z_m$ . Our final result is obtained by inserting Eq. (44) into Eq. (36) and adding the corresponding expression for  $k_2^{\mathbf{p}}(a)$ . Thus,

$$k^{B}(a) = (g_{12}/g_{1}g_{2}) 2\pi (2\pi\mu_{12}kT)^{\frac{1}{2}}(z_{2}-z_{1})z_{2}^{2} \\ \times [1-\exp(-B_{m}/kT)] \\ \times \{m_{1}^{-1}\{a_{1-2}(F_{p}^{1-}(z_{2})+F_{l}^{1-}(z_{2}))\exp(\epsilon/kT) \\ +a_{1+2}(F_{p}^{1+}(z_{2})+F_{l}^{1+}(z_{2}))[\exp(\epsilon/kT)-1]\} \\ +m_{2}^{-1}[a_{2-2}(F_{p}^{2-}(z_{2})+F_{l}^{2-}(z_{2}))\exp(\epsilon/kT) \\ +a_{2+2}(F_{p}^{2+}(z_{2})+F_{l}^{2+}(z_{2}))[\exp(\epsilon/kT)-1]\}\}.$$
(45)

This is a rather formidable expression, but considering the complexity of the problem we might have expected worse. Actually, the only real complication is that involved in integrating Eq. (41a) and (41b) to obtain the F's. This must be done either graphically or numerically. In cases where a rough estimate of the rate will suffice, the F's may be taken equal to unity.

The most important difference between the calculation made above and the one carried out by Wigner is that we have included explicitly, both the effect of the rotational barrier and the van der Waals force. This leads to a considerably more complicated temperature dependence than the simple  $T^{-1}$  law found by Wigner, as well as a substantial reduction in the rate constant at low temperatures.

It is worth nothing that our expression for the barrier rate constant contains a good deal of the correct mechanics of the problem. What is missing is the consideration of trajectories which cross  $S^{\mathbf{B}}$  more than once.

#### Variational Rate

To obtain the variational rate constant  $k^{\nu}(a)$  we simply add the available energy rate constant  $k^{A}(a)$ and the "barrier" rate constant  $k^{B}(a)$ , and minimize with respect to variations of the parameter a. While in principle this can be done analytically, in practice it has been found more convenient to simply calculate  $k^{A}(a) +$  $k^{B}(a)$  for several values of a and locate the minimum graphically.

The actual calculations of  $k^{A}(a)$  and  $k^{B}(a)$  were programmed for an IBM 650 computer for which this



FIG. 7. Curves illustrating the method used to determine the variational rate constant  $k^{V}$  for the process  $O+O+A=O_2$  ( ${}^{3}\Sigma_{0}^{-}$ )+A for several values of kT/D where D is the binding energy of  $O_2({}^{3}\Sigma_{0}^{-})$ . Note that, as kT/D increases, the position of the minimum corresponding to the "variational" rate constant moves from a=0 toward  $a=a_{-}+z_{m}/2$ , beyond which point the "barrier" rate constant  $k^{B}(a)$  is essentially 0.

problem is trivial. Only the case of symmetrical molecules, i.e.,  $A_1=A_2$ , was treated, and the interaction potential  $V_{12}$  was assumed to have the Morse form. A detailed discussion of this potential and a summary of the constants employed is given in part I of Appendix A. The potential  $V_{13}$  between the third body and a recombining atom was assumed to have the Lennard-Jones form at large separation and the Mason-Vanderslice<sup>4</sup> form at small separation. The two forms were smoothed graphically in the region of overlap. A detailed discussion of these potentials and a summary of the parameters used is given in parts II and III of Appendix A.

Some typical results, which serve to illustrate the procedure for locating the minimum rate constant are shown in Fig. 7 for the case

$$O+O+A\rightarrow O_2(^{3}\Sigma_{g})+A$$

In this figure, the rate constants  $k^{(a)}$ ,  $k^{(B)}(a)$  and  $k^{(a)} + k^{(B)}(a)$  are plotted as functions of  $a^2/(a_++z_m/2)^2$  for several values of the dimensionless temperature kT/D. It can be seen that for  $kT/D\ll 1$  the best value of  $a/(a_++z_m/2)$  is zero, in which case  $k^v \approx k^{(B)}(0)$ , while for  $kT/D\gg 1$  the best value of  $a/(a_-+z_m/2)$  is

unity, in which case  $k^{\nu} \approx k^{A}(a_{-}+z_{m}/2)$ . As shown in Fig. 8, the transition region in which  $k^{A}(a)$  and  $k^{B}(a)$  are simultaneously important is relatively narrow, and in practice  $k^{\nu}$  can easily be interpolated so that it is unnecessary to carry out the detailed analysis illustrated in Fig. 7.

An analysis similar to that just described was also carried out for the case,

$$I+I+A\rightarrow I_2({}^1\Sigma_g^+)+A,$$

and the results were essentially identical except that the crossing point for  $k^{\mathbf{B}}(0)$  and  $k^{\mathbf{A}}(a_{-}+z_{m}/2)$  occurred at  $kT/D\approx 3$ .

From a practical point of view, the temperature range of primary interest is that for which kT/D < 1. Since the preceding analysis showed that in this range  $k^{v} = k^{B}(0)$  for both iodine and oxygen, it seems fairly safe to conclude that this will be the case in general and, thus, the properties of the "barrier" rate constant are of special importance. In this connection, it is of interest to compare the relative contributions to  $k^{B}(0)$  made by vibrational and rotational transitions. This is done in Fig. 9, where  $k_{pB}(0)$  and  $k_{lB}(0)$  are plotted along with  $k^{B}(0)$  as functions of kT/D. It can be seen that at low temperatures the major contribution to  $k^{B}(0)$ arises from  $k_{p}B(0)$ , while at high temperatures the major contribution is from  $k_{l^{B}}(0)$ . The ratio of  $k_{l^{B}}(0)/k_{p^{B}}(0)$  varies approximately as  $T^{\frac{1}{2}}$ , and it can be shown that this is a result of including the effect of the rotational barrier in the calculations. In the Wigner calculation, which neglects the rotational barrier, there is no difference in the temperature dependence of



FIG. 8. The curve labeled  $k^V$  shows the variational rate constant for the process  $O+O+A=O_2({}^{2}\Sigma_{g}^{-})+A$  as a function of kT/D, where D is the binding energy of  $O_2({}^{3}\Sigma_{g}^{-})$ . The curves labeled  $k^B(0)$  and  $k^A(a_-+z_m/2)$  are, respectively, the low and high temperature asymptotes for  $k^V$ . Note that  $k^V$  is quite well approximated by the smaller of  $k^B(0)$  and  $k^A(a_-+z_m/2)$  and can easily be interpolated in the transition region.

<sup>&</sup>lt;sup>4</sup> E. A. Mason and J. T. Vanderslice, J. Chem. Phys. 28, 432 (1958).

the vibrational and rotational contributions. The reason for pointing out this effect is that, as will be seen later, the experiments show a stronger negative temperature dependence than the theory, and it is tempting to speculate that at least part of the difference may be due to the fact that rotational transitions are less important than the theory predicts. This would be the case if the true three-body potential were more nearly spherically symmetric than the dumbbell shape assumed.

Figure 9 also shows that the barrier rate constant is a considerably better bound than the Wigner rate constant, especially at low temperatures. This is a simple result of the fact that the rotational barrier limits the number of trajectories which can reach the surface  $H_{12}=0$  from the free state. An interesting project would be to calculate this correction. It would also be of interest to consider the general case where  $H_{12}$ is set equal to an arbitrary constant. This would give bounds on the frequency of vibrational and rotational transitions in molecules.

# IV. ELECTRONIC TRANSITIONS

Before we can make a meaningful comparison of theory and experiment, we must first consider the effect of transitions between the various bound electronic states of a molecule, which are degenerate in the free state. This is necessary because what is usually measured in experiments is either the depopulation of the free state or the population of the ground state, and the existence of intermediate electronic states can provide alternative paths by which this can occur. Such a path is the chain reaction,

$$\begin{array}{c} k_{fi} \\ A + A + M \longrightarrow A_2^i + M \end{array}$$
 (46a)

$$\begin{array}{c} k_{i0} \\ A_2{}^i + X \longrightarrow A_2 + X, \end{array}$$
 (46b)

where  $A_2^i$  denotes a molecule in an intermediate electronic state.

The general solution of these equations involves considerable complication and will not be undertaken here. Instead, we shall consider the two limiting cases in which either the reaction,

$$\begin{array}{c} k_{ij} \\ A_2^i + M \longrightarrow A + A + M, \end{array}$$
(47a)

or the reaction

$$\begin{array}{c} k_{i0} \\ A_2{}^i + X \longrightarrow A_2 + X \end{array}$$
 (47b)

dominates in depopulating  $A_2^i$ . If reaction (47a) is dominant, then we may assume reaction (46a) is in equilibrium and the over-all reaction rate is

$$R_{fi0} = k_{fi0} [A]^{2} [M], \quad k_{fi0} \ll k_{fi}, \tag{48}$$



FIG. 9. Recombination rate constants for  $O+O+A\rightarrow O_2$  $({}^{3}\Sigma_{g}^{-})+A$ . The curve labeled  $k^B(0)$  shows the "barrier" rate constant evaluated for a=0. The curves labeled  $k_p^B(0)$  and  $k_1^B(0)$  show, respectively, the contributions to  $k^B(0)$  due to vibrational and rotational transitions. Note that at low temperatures vibrational transitions are dominant, while at high temperatures rotational transitions are dominant. The curve labeled  $k^w$  shows the Wigner rate constant for comparison.

where

$$k_{fi0} = (k_{i0}K_{fi}^{-1})([X]/[M])$$
(49)

is the effective three-body rate constant for the over-all reaction with M as the third body and  $K_{fi}$  is the equilibrium constant for reaction (47a). If the reaction (47b) is dominant, then we can assume  $A_2^i$  is in a steady state of near zero concentration, and the over-all reaction rate is

$$R_{fi0} = k_{fi} [A]^{2} [M], \quad k_{fi} \ll k_{fi0}.$$
(50)

Thus, we see that the rate-limiting rate constant is the smaller of  $k_{fi}$  and  $k_{fi0}$ .

For our subsequent discussion, it is convenient to express  $k_{fi0}$  in terms of the cross section  $\sigma_e$  for electronic transitions, from the intermediate to ground state. A straightforward calculation involving essentially only the evaluation of  $K_{fi}$  leads to the result,

$$k_{fi0} = \sigma_e (2D_i/\mu)^{\frac{1}{2}} (g_i/g_f) (8\pi r_i^2/\beta_i) \chi_i \{ [X]/[M] \}, (51)$$

where

$$\chi_{i} = 2(hc\omega_{i}/D_{i}) [\cosh(D_{i}/kT) - 1] [1 - \exp(-hc\omega_{i}/kT)]^{-1}$$
(52)

is a dimensionless factor shown as a function of temperature in Fig. 10,  $g_i/g_f$  is the ratio of the electronic degeneracy of the intermediate and free states, and  $\mu$ is the reduced mass for a collision of A<sub>2</sub> and X. The constants  $D_i$ ,  $\omega_i$ ,  $r_i$ , and  $\beta_i$  are, respectively, the binding energy, vibrational constant, equilibrium separation, and decay constant for A<sub>2</sub><sup>i</sup> and are tabulated in Appendix A for a few molecules of interest.



FIG. 10. Curves of the function  $\chi$ , defined in Eq. (53), as a function of kT/D for two values of the parameter  $hc\omega/D$ . This function determines the temperature dependence of recombination via the chain mechanism (46) in cases where the electronic transition is the rate-limiting step. The left scale should be used for the two curves on the left and the right scale for the two curves on the right.

To obtain numerical values for  $k_{fi0}$ , we require a knowledge of the cross section  $\sigma_e$  for electronic transitions from the intermediate to ground state. These transitions usually involve spin flips and are expected to be very improbable except in cases where atom exchange occurs. Fortunately, due to the exceedingly steep temperature dependence of the factor  $\chi_i$ , all we need for our present purposes is an estimate of the cross section good to one, or two orders of magnitude. We have, therefore, assumed that only atoms of the recombining species induce electronic transitions and that the cross section for the reaction is of the order of  $g_0/g_f$  times the kinetic cross section. The factor  $g_0/g_f$ is the ratio of the electronic degeneracy of the ground and free states, and is included on the loose argument that for a reaction to occur the reacting atoms must be appropriately oriented. The only other unknown factor in  $k_{fi0}$  is the ratio [X]/[M] which, with our assumption that X=A, is time-dependent. Again, because of the extremely steep temperature dependence of the factor  $\chi_i$ , this complication can be glossed over for the present and we have simply taken  $[X]/[M] = 10^{-2}$ , which is typical of all the experiments we shall discuss.

# V. COMPARISON OF THEORY AND EXPERIMENT

## **Temperature Dependence**

The rate constants for recombination of iodine, bromine, oxygen, and nitrogen atoms in the presence

of argon have been calculated as a function of the temperature for both the direct and chain mechanisms and are shown in Figs. 11-14 along with the available experimental data. The curves labeled  $f \rightarrow 0, f \rightarrow 1, \text{ etc.},$ refer to direct recombination of atoms into the bound electronic states, 1, 2, etc., identified in the figures. The curves labeled  $1 \rightarrow 0, 2 \rightarrow 0$ , etc., refer to recombination to the ground state via the chain mechanism under conditions where the rate-limiting step is assumed to be the transition between electronic states. In this connection, note that the curves are shown as solid lines where the corresponding process is the ratelimiting step and are dashed otherwise. Also, note that the crossing points are uncertain due to our ignorance of the cross sections for electronic transitions, although a change of one or two orders of magnitude is required to produce an appreciable effect. The curves labeled  $\Sigma$ represent the sum of all processes leading to the ground



FIG. 11. Three-body recombination rate constants for I+I+ A  $\rightarrow$  I<sub>2</sub>+A as a function of  $kT/D_0$ , where  $D_0$  is the binding energy of I<sub>2</sub>( $\Sigma_0^+$ ). The curves labeled  $f \rightarrow 0(\Sigma)$  and  $f \rightarrow 1$  are the rate con-stants for direct recombination to the  ${}^{1}\Sigma_0^+$  and  ${}^{3}\Pi_{1u}$  states of I<sub>2</sub>. These curves have been cut off at  $\epsilon/kT=1$ , where  $\epsilon$  is the depth of the van der Waals potential, since the theory is no longer applicable below this point. The curve labeled  $1 \rightarrow 0$  is an estimate of the effective rate constant for transitions from the  ${}^{3}\Pi_{1u}$  to the  $\Sigma_{g}^{+}$  state. Note that in the range  $\epsilon/kT \leq 1$  the transition  $1 \rightarrow 0$  is always the rate-limiting step for recombination to the 0 state via the chain mechanism Eq. (46). To indicate this, we have used a solid line for the curve  $1\rightarrow 0$  and a dashed line for the curve  $f \rightarrow 1$ . Curve (1) shows the low temperature experimental data obtained in flash photolysis experiments.<sup>5,6</sup> Curve (2) shows the high temperature recombination rate constants deduced from dissociation rates measured in shock tubes.7 The experimental data lie very close to the theoretical upper bound  $f \rightarrow \hat{1}(\Sigma)$  at low temperatures but exhibit a steeper temperature dependence than the theory. Possible explanations for this are discussed in the text.

<sup>&</sup>lt;sup>5</sup> D. L. Bunker and N. Davidson, J. Am. Chem. Soc. 80, 5085 (1958).

<sup>&</sup>lt;sup>6</sup> Strong, Chien, Graf, and Willard, J. Chem. Phys. 26, 1287

<sup>(1957).</sup> <sup>7</sup> Britton, Davidson, Gehman, and Schott, J. Chem. Phys. 25, 804 (1956).

state, and it is these with which the experimental data should be compared.

In making the comparison of theory and experiment, it should be remembered that the theory gives a rigorous upper bound to the rate constant. Thus, we expect the observed rate constants to fall below the  $\Sigma$ curves. It is interesting to note that at low temperatures all the experimental data lie quite close to the theoretical bound. This is shown more clearly in Fig. 15 where we have plotted the ratio of the observed rate constants to the upper bound represented by the  $\Sigma$ curve as a function of  $kT/D_0$ , where  $D_0$  is the binding energy of the ground state. Although points for oxygen and nitrogen and a portion of the bromine curve actually lie above the bound, this is not considered serious, since a rather large error is quoted for the oxygen result, the nitrogen result disagrees with another measurement, and the bromine data are uncor-



FIG. 12. Recombination rate constants for  $Br+Br+A\rightarrow Br_2+A$ as a function of  $kT/D_0$ , where  $D_0$  is the binding energy of Br<sub>2</sub>  $({}^{1}\Sigma_{g}{}^{+})$ . The curves marked  $f \rightarrow 0$  and  $f \rightarrow 1$  are the rate constants for direct recombination to the  $\Sigma_{\rho}^{+}$  and  $\Pi_{iu}$  states of Br. These curves have been cut off at the point  $\epsilon/kT=1$ , where  $\epsilon$  is the depth of the van der Waals potential, since the theory is no longer applicable below this point. The curve labeled  $1\rightarrow 0$  is an estimate of the effective rate constant for transitions from the  ${}^{3}\Pi_{1u}$  to the  ${}^{1}\Sigma_{g}$  + state. The portions of the curves shown as solid lines indicate the regions in which the corresponding process is the rate-limiting step in recombination to the 0 state via the chain mechanism, Eq. (46). The curve labeled  $\Sigma$  shows the rate constant for recombination to the 0 state via both direct and chain mechanisms. Curve (3) shows the low temperature experimental data obtained in flash photolysis experiments.<sup>6</sup> Curve (4) shows the high temperature recombination rate constants deduced from dissociation rates measured in shock tubes.<sup>8,9</sup> Although the experimental rate constant exceeds the theoretical upper bound  $\Sigma$  at low temperatures, there is a strong possibility that the experimental results may be high, and this is not regarded as a serious disagreement. As in the case of iodine, the experimental data show a steeper temperature dependence than the theoretical bound. Reasons for this are discussed in the text.



FIG. 13. Three-body recombination rate constants for  $O+O+A \rightarrow O_2+A$  as a function of  $kT/D_0$ , where  $D_0$  is the binding energy of  $O_2(^{2}\mathcal{E}_{\sigma}^{-})$ . The curves labeled  $f\rightarrow 0$ ,  $f\rightarrow 1$ ,  $f\rightarrow 2$ , and  $f\rightarrow 3$  are the rate constants for direct recombination to the  $^{3}\Sigma_{\sigma}^{-1}\Delta_{\sigma}^{-1}\Sigma_{\sigma}^{-1}$ ,  $^{3}\Delta_{\sigma}^{-1}\Sigma_{\sigma}^{-1}$ ,  $^{3}\Delta_{\sigma}^{-1}\Sigma_{\sigma}^{-1}\Sigma_{\sigma}^{-1}$ ,  $^{3}\Delta_{\sigma}^{-1}\Sigma_{\sigma}^{-1}$ ,  $^{3}\Delta_{\sigma}^{-1}\Sigma_{\sigma}^{-1}$ ,  $^{3}\Delta_{\sigma}^{-1}\Sigma_{\sigma}^{-1}\Sigma_{\sigma}^{-1}$ ,  $^{3}\Delta_{\sigma}^{-1}\Sigma_{\sigma}^{-1}\Sigma_{\sigma}^{-1}$ ,  $^{3}\Delta_{\sigma}^{-1}\Sigma_{$ 

rected for the effect of  $Br_2$  as catalyst and are expected to be "high."

Assuming our approximation to the three-body potential is at all reasonable, we can draw the tentative conclusion that recrossing of the "barrier" surface by single trajectories, (i.e., recombination and dissociation in a single collision) is a small effect at low temperatures. This would not be an unreasonable thing to expect, since at low temperatures, the phase volume associated with bound states tremendously outweighs that associated with free states and, thus, a trajectory which once crosses the barrier surface has a good chance of coming out in a bound state.

At high temperatures, the observations do fall somewhat below the theoretical bound. The interesting feature to note in this region is that the ratios of  $k_{\rm exp}/k_{\Sigma}$ for all the species studied appear to lie more or less on a smooth curve when plotted as a function of  $kT/D_0$ .

<sup>&</sup>lt;sup>10</sup> C. B. Kretschmer, Aerojet Report 1611, Azusa, California, (1959). <sup>11</sup> S. R. Byron, J. Chem. Phys. **30**, 1380 (1959).

 <sup>&</sup>lt;sup>8</sup> D. Britton and N. Davidson, J. Chem. Phys. 25, 810 (1956).
 <sup>11</sup> S. R. B
 <sup>9</sup> H. B. Palmer and D. F. Hornig, J. Chem. Phys. 26, 98 (1957).
 <sup>12</sup> M. Car

<sup>&</sup>lt;sup>12</sup> M. Camac, private communication.



FIG. 14. Three-body recombination rate constants for N+N+ $A \rightarrow N_2 + A$  as a function of  $kT/D_0$ , where  $D_0$  is the binding energy of  $N_2({}^{1}\Sigma_g{}^{+})$ . The curves labeled  $f \rightarrow 0$  and  $f \rightarrow 1$  are the rate constants for direct recombination to the  ${}^{1}\Sigma_{g}^{+}$  and  ${}^{3}\Sigma_{g}^{+}$  states of N<sub>2</sub>. The curve labeled  $1 \rightarrow 0$  is an estimate of the effective rate constants for transition from the  ${}^{3}\Sigma_{g}^{+}$  to the  ${}^{1}\Sigma_{g}^{+}$  state. The portions of the curves shown as solid lines indicate the regions in which the corresponding process is the rate-limiting step in recombination to the 0 state via the chain mechanism Eq. (46). The curve labeled  $\Sigma$  shows the rate constant for recombination to the 0 state via both direct and chain mechanisms. The points (7) and (8) show the results of flow experiments in which the atom concentration was determined by titrating with NO.13,14 The two experiments give values which bracket the theoretical upper bound  $\Sigma$ .

This suggests that the mechanism responsible for depressing the observed rate constant below the theoretical bound depends in the first approximation only on the binding energy of the ground state. It is not surprising that the correlation should be with the ground state binding energy since for iodine, bromine, and oxygen the ground state plays the dominant role. At the present time, it does not seem unreasonable to suppose that other molecules will exhibit a similar departure from the theoretical upper bound, and thus, we may use the observed correlation as a basis for making fairly precise theoretical predictions of recombination rates. In this connection, it will be of considerable interest to see if the recombination rate of nitrogen atoms follows the same pattern at high temperatures. Note, however, that in nitrogen a correction may have to be made for the increased importance of recombination via the chain mechanism.

There are two possible explanations for the decrease in the ratio of  $k_{exp}/k_{\Sigma}$  with increasing temperature:

First, multiple crossings of the barrier surface can be expected to become more important as the temperature increases. Since this is an effect which is probably

associated with the ratio of free to bound states, it is reasonable to expect a dependence on  $kT/D_0$ . The question of whether this effect is important is one which could be answered quite easily by Monte Carlo trajectory calculations, and it is proposed as a very important problem for those working in this area.

Second, our approximation to the three-body potential is certainly rather poor. As an example of how the three-body potential can affect the temperature dependence of the rate constant, we recall the previous discussion of the difference in the temperature dependence of rotational and vibrational transitions. In this discussion, it was noted that the major contribution to the rate constant at high temperatures came from rotational transitions and that these are dependent on the asymmetry of the three-body potential. A more nearly symmetric potential would result in a smaller contribution from rotational transitions and,



FIG. 15. Ratio of experimental three-body recombination rate constants  $k_{exp}$  to theoretical upper bounds  $k_{\Sigma}$  as a function of  $kT/D_0$ , where  $D_0$  is the ground state binding energy. In all cases, the third body is argon. Curve (1) summarizes the results of flash photolysis experiments on recombination of iodine atoms.<sup>5,6</sup> Curve (2) summarizes the results of shock tube experiments on the dissociation of iodine.<sup>7</sup> Curve (3) summarizes the results of flash photolysis experiments on the recombination of bromine atoms.<sup>6</sup> Curve (4) summarizes the results of shock tube experiments on the dissociation of bromine.<sup>8,9</sup> Point (5) is the result of discharge experiments on the recombination of oxygen atoms in which the atom concentration was determined from the photon vield of the reaction NO+O $\rightarrow$ NO<sub>2</sub>+hv.<sup>10</sup> Curve (6) summarizes the results of shock tube experiments on the dissociation of oxygen.<sup>11,12</sup> Points (7) and (8) are the results of flow experiments on the recombination of nitrogen atoms in which the atom con-centration was determined by titrating with NO.<sup>13,14</sup> At low temperatures, the experimental results scatter about the theo-retical upper bound. The fact that some of the data lie slightly above the bound is not considered serious at present due to the likelihood of experimental errors of this magnitude. At high temperatures, the experimental data fall away from the bound in a more-or-less smooth manner, which suggests that the mech-anism responsible is nonspecific and may well be the same for all molecules. If this is the case, the theory can be empirically corrected to give recombination rate constants to about a factor of 2. Possible explanations of this effect and suggestions for improving the theory are given in the text.

<sup>&</sup>lt;sup>13</sup> Herron, Franklin, Bradt, and Dibeler, J. Chem. Phys. 30,

<sup>879 (1959).</sup> <sup>14</sup> Hartech, Reeves, and Mannella, J. Chem. Phys. 29, 608

hence, a steeper temperature dependence of the rate constant.

The above discussion suggests that the study of reaction rates can be a means of investigating threebody potentials. A possible approach to the problem would be to represent the three-body interaction as an expansion in cylindrical harmonics with unknown coefficients to be determined by comparison with experiment. It is reasonable to suppose that such an expansion would converge rapidly so the number of undetermined coefficients might be quite small. It would be of considerable interest to observe the form of the various terms in the expansion. We already know, for example, that there would be no rotational contribution from the spherically symmetric part.

## **Atomic Number Dependence**

A further comparison of theory and experiment is shown in Table I in which we have compared the theoretical bounds with the experimental rate constants for the recombination of iodine in the presence of noble gases.<sup>15,16</sup> The results of two experiments are shown, and it can be seen that the theory reproduces the trend of the observations almost perfectly. Although the observations are slightly higher than the bound given by the theory, the discrepancy is probably within the experimental error. Furthermore, a comparison of the tabulated argon results with more recent results, shown graphically in Fig. 11, indicates that the tabulated values may be slightly high.

It should be noted that the increase in the theoretical rate constant with atomic number is not a mass but a size effect. The theory is independent of the mass of the third body. The mass effect results in a decrease of the rate constant with increasing atomic number due to the slower velocity of the heavier particles. At room temperature, where the observations were made, the size effect is governed almost entirely by the van der Waals force, and since this was interpolated from measurements on noble gases there is room for improvement here.

At this point, it seems appropriate to inject a few remarks on the probable effect of other third bodies on the recombination reaction. It was already noted that the theoretical rate constants are independent of third body mass. They are also independent of the internal complexity of the third body as long as its internal state does not affect the external force field. We expect the present theory to share the success of the Bunker and Davidson theory<sup>17</sup> in explaining the relative efficiencies of complex catalysts at low temperatures since the van der Waals force enters in much the same way. It is also

TABLE I. Comparison of theoretical upper bounds,  $k_{\Sigma}$ , with observed rate constants for recombination of iodine atoms in the presence of noble gases. The observations are those of Christie, Harrison, Norrish, and Porter, <sup>15</sup>  $k_{CHNP}$ , and Russell and Simons, <sup>16</sup>  $k_{RS}$ . The theoretical bounds reproduce the trend of the observations to the accuracy with which the two experiments agree. Although the observed rate constants are slightly higher than the bounds, the discrepancy is probably within the experimental errors. The units are  $10^{-33} \sec^{-1} \operatorname{cm}^6$  molecules<sup>-2</sup>.

Catalyst	$k_{\Sigma}$	k <sub>CHNP</sub>	$k_{\rm RS}$	$k_{\rm CHNP}/k_{\Sigma}$	$k_{\rm RS}/k_{\Sigma}$	
He Ne A Kr	3.0 4.3 7.5 9.1	3.4 4.6 9.2 11.3	4.7 5.0 10.0	1.1 1.1 1.2 1.2	1.6 1.2 1.4	
Xe	11.4	15.0		1.3		

expected that attractive atoms will have a somewhat higher intrinsic efficiency as third bodies than repulsive ones since a larger region of configuration space is open to them. It should be noted, however, that in most cases the electronic degeneracy of attractive configurations is small compared to that of repulsive configurations so the over-all effect on the rate constant will be considerably diminished. The important effect in connection with attractive atoms is expected to be their ability to induce electronic transitions between the various bound states of a molecule by exchange collisions. Attractive third bodies with internal degrees of freedom have not been considered in any detail, but they should be very efficient due to the high probability of forming long-lived complexes.

## VI. CONCLUDING REMARKS

Considering the simple "trial" surface used and the crude approximation to the three-body potential assumed, the comparison between theory and experiment is quite encouraging. At low temperatures, the observed recombination rate constants lie very near the predicted upper bounds, while at high temperatures they fall away from the bounds in a relatively smooth manner that can be qualitatively explained in terms of various approximations contained in the theory. Among the most important problems requiring investigation in connection with these approximations are: (1) the representation of the three-body potential, (2) the effect of multiple crossing of the "trial" surface by single trajectories, and (3) the treatment of electronic transitions between bound states. Improvement in the treatment of all these problems is certainly feasible, and some possible approaches have been mentioned. There is also the possibility of reducing the theoretical bound through the systematic investigation of other and perhaps more complicated trial surfaces. In view of the many opportunities available for refinement of the theory, it does not seem unreasonable to hope that a very satisfactory description of threebody recombination and dissociation can be obtained with the present approach.

<sup>&</sup>lt;sup>15</sup> Christie, Harrison, Norrish, and Porter, Proc. Roy. Soc. (London) A231, 446 (1955). <sup>16</sup> K. E. Russell and J. Simons, Proc. Roy. Soc. (London) A217,

<sup>&</sup>lt;sup>16</sup> K. E. Russell and J. Simons, Proc. Roy. Soc. (London) **A217**, 271 (1953).

<sup>&</sup>lt;sup>17</sup> D. L. Bunker and N. Davidson, J. Am. Chem. Soc. **80**, 5090 (1958).

TABLE II. Summary of parameters for the Morse potential.\*

Molecule	μ	State	D <sub>M</sub> /k °K	$\stackrel{\beta_{\mathbf{M}}}{A^{-1}}$	r. A	β <sub>M</sub> r.	ω cm <sup>-1</sup>
N <sub>2</sub>	7	$\frac{1\Sigma_g}{3\Sigma_u}^+$	1.15 <sup>5</sup> 4.25 <sup>4</sup>	2.69 2.74	1.09 1.29	2.94 3.54	2360 1460
O2	8	$3\Sigma_{g}^{-1}\Delta_{g}$ $1\Delta_{g}^{1}\Sigma_{g}^{+}$ $3\Sigma_{u}^{+}$	$\begin{array}{c} 6.01^4 \\ 4.86^4 \\ 4.11^4 \\ 8.16^3 \end{array}$	2.65 2.82 2.93 3.74	$1.21 \\ 1.22 \\ 1.23 \\ 1.42$	3.20 3.42 3.59 5.3	1580 1509 1433 819
Br <sub>2</sub>	40	${}^{1}\Sigma_{g}^{+}$ ${}^{3}\Pi_{1u}$	2.314 3.243	1.94 2.80	2.28 3.1	4.44 8.7	323 171
I <sub>2</sub>	63.5	${}^{1}\Sigma_{g}^{+}$ ${}^{3}\Pi_{1u}$	1.81 <sup>4</sup> 9.65 <sup>2</sup>	1.86 1.66	2.67 5.9	4.96 9.8	215 44

<sup>a</sup> G. Herzberg, Spectra of Diatomic Molecules (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950).

In concluding, we should like to point out the relationship of the present variational theory of reaction rates to the "statistical" theory previously proposed by the author.<sup>1</sup> The two theories are in a sense complimentary, since the trial surfaces of the variational theory form appropriate boundaries for the collision complex of the statistical theory. In fact, it was the problem of defining the boundaries of the collision complex which led to the development of the variational theory. Coupling of the two theories provides a reasonable method for estimating the rate constants in cases where two or more trial surfaces are found which give comparable bounds to the reaction rate. For example, we have already employed the ideas of the statistical theory in a qualitative manner in arguing that multiple crossing of the barrier surface by single trajectories should be unimportant at low temperatures. However, because the statistical theory is non-



FIG. 16. Curves showing effective Morse potential for several values of angular momentum.



FIG. 17. Curves relate various parameters identified in Fig. 16. The curve labeled (-V/D) was obtained from Eq. (A1). The curves labeled B/D were obtained by substituting Eq. (A1) into Eq. (16). The curve labeled  $B_m/D$  is the locus of the maxima of the B/D curves.

rigorous and leads to involved calculations, it is felt that quantitative treatment of the coupling problem should await the solution to the more important problems in connection with the variational theory.



FIG. 18. Curves showing the relation between position  $z_2$  of the maximum in the function  $|dB/dz| \exp(-B/kT)$  and the temperature T. The curves were obtained by combining Eqs. (A1), (16), and (43).



FIG. 19. Curves showing the relation between  $(z_2-z_1)$  and  $z_2$ . The curves were obtained by numerical solution of Eq. (42), with  $u_{12} = V_M/kT$ .

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#### APPENDIX

#### I. Morse Potential

The Morse potential is described by the equation,

$$V_{M}(r) = D_{M}\{\{1 - \exp[-\beta_{M}(r - r_{e})]\}^{2} - 1\}.$$
 (A1)

The corresponding effective potential is

$$V_{\rm M}'(r) = V_{\rm M}(r) + l^2/2\mu r^2,$$
 (A2)

where l is the angular momentum of the molecules and the constants  $D_M$ ,  $\beta_M$ ,  $r_e$ , and  $\mu$  are tabulated for the

 
 TABLE III. Summary of parameters for Mason-Vanderslice potential.



FIG. 20. Mason-Vanderslice potential for several values of the parameter *a*. The curves are plots of Eq. (A3) with  $\beta' = \beta_{MV}$ .

molecular states of interest in the present work in Table II. The general form of the effective potential is shown in Fig. 16 for several values of l. Note there is a maximum value of angular momentum  $l_m$  for which the effective potential has a relative minimum.

Some useful curves relating various parameters appearing in the theory are shown in Figs. 17–19. These were obtained by inserting Eq. (A1) into the defining equations.

#### **II. Mason-Vanderslice Potential**

For homonuclear interactions, the Mason-Vanderslice potential<sup>4</sup> may be written in the form,

$$V_{\rm MV}(r) = D_{\rm MV} \exp[-\beta' r - 2\alpha \exp(-\beta' r/\alpha)], \quad (A3)$$

where

$$\beta' = (1 - V_{MV}/D_{MV})\beta_{MV}. \tag{A4}$$

 $D_{MV}$ ,  $\beta_{MV}$ , and  $\alpha$  are constants related to the atomic properties of the interacting atoms, and a summary

TABLE IV. Summary of parameters for Lennard-Jones potential. The values for the noble gases were taken from reference 19. The values for the remaining atoms were obtained by interpolation on Z.

Atom	A	$D_{\rm MV}/k$ °K	$\beta_{MV} A^{-1}$	α	Atom	A	Z	e/k	σ	
He Ne	4 20	4.11 <sup>6</sup> 1.58 <sup>7</sup>	4.83 4.24	1.50 1.54	 He Ne	4 20	2 10	10 33	2.6 2.79	
A	40	1.537	3.10	2.18	A	40	18	120	3.42	
Kr	84	2.387	2.74	2.39	Kr	84	36	173	3.00	
Xe	131	2.71'	2.38	2.24	Xe	131	54	223	4.04	
N	14	4.966	2.84	1.55	N	14	7	25	2.7	
0	16	5.066	2.67	1.24	0	16	8	30	2.7	
Br	80	1.657	2.31	2.18	Br	80	35	170	3.6	
I	127	2.037	2.08	2.31	I	127	53	220	4.0	



FIG. 21. Curve showing the relation between the position r of the maxima in the function  $|dV_{LJ}/dr| \exp(-V_{LJ}/kT)$  and the temperature T. The curve was obtained by inserting Eq. (A5) into Eq. (35).

of values for the atoms of interest in the present work is given in Table III. Note that, since the definition of  $\beta'$ involves  $V_{MV}$ , Eq. (A3) gives only an implicit definition of  $V_{MV}$  and this produces some complication. Fortunately, in all cases of interest in the present work,  $V_{MV}/D_{MV}\ll 1$  and we can, therefore, set  $\beta' \approx \beta_{MV}$ Figure 20 shows curves of  $V_{MV}/D_{MV}$  for  $\beta' = \beta_{MV}$  as a function of  $\beta_{MV}r$  for several values of  $\alpha$ . At low energies, the curves are all asymptotic to a simple exponential.

For heteronuclear interactions, Mason and Vanderslice suggest using the geometric mean of the two potentials for the homonuclear interaction of the atoms involved.

To calculate the barrier rate constant, we require the value of the separation  $a_{-}$  at which  $| dV_{MV}/dr |$  $\exp(-V_{MV}/kT)$  has a maximum. For  $\beta_{MV}r \ge \alpha$ , which is the case of interest, this occurs to an excellent approximation at the point  $V_{MV} = kT$ . Thus, for the homonuclear case,  $a_{-}$  may be obtained directly from the curves in Fig. 20. For the heteronuclear case, the appropriate potential must first be computed in order to determine  $a_{-}$ .

## **III.** Lennard-Jones Potential

To represent the van der Waals interaction, we have used the Lennard-Jones potential, which for homonuclear interactions has the form,

$$V_{\rm LJ} = 4\epsilon [(\sigma/r)^{12} - (\sigma/r)^6]. \tag{A5}$$

The constants  $\epsilon$  and  $\sigma$  for the atoms of interest in the present paper are given in Table IV.

For the heteronuclear interactions, the combination rules

$$\epsilon_{12} = (\epsilon_1 \epsilon_2)^{\frac{1}{2}} \tag{A6}$$

and

$$\sigma_{12} = \frac{1}{2}(\sigma_1 + \sigma_2) \tag{A7}$$

are recommended by Hirschfelder, Curtiss, and Bird.18

To calculate the barrier rate constant, we require the separations  $a_{-}$  and  $a_{+}$  at which

$$| dV_{LJ}/dr | \exp(-V_{LJ}/kT)$$

has maxima. These may be obtained from the graph in Fig. 21 which represents the solution of Eq. (35).

It should be noted that the values of  $a_{-}$  obtained from the Lennard-Jones and Mason-Vanderslice potentials do not join smoothly. In the present calculations, smoothing was done graphically.

<sup>18</sup> Hirshfelder, Curtiss, and Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954).