PHYSICAL REVIEW VOLUME 107, NUMBER 2 JULY 15, 1957

Theoretical Treatment of the Kinetics of Diffusion-Limited Reactions

T. R. Waite
Bell Telephone Laboratories, Murray Hill, New Jersey

(Received April 12, 1957)

The problem of the kinetics of the diffusion-limited reaction $A+B\rightarrow AB$ has been formulated in terms of the pair probability densities of the reacting particles (every A taken with every B). The alteration of these pair densities due to diffusion and reaction have been considered. The competition of every A for every B and the removal of particles from the system upon reaction have been appropriately accounted for. The formulation leads to a set of coupled differential equations that can be solved for a variety of boundary conditions. The problem has been solved in detail for a random initial distribution. The rate of reaction at any time is just the probable rate at which a single A and a single B diffuse together (with an appropriate boundary condition for reaction on close approach) multiplied by the product of the number of A's and the number of B's present at that particular time. The rate of the reaction $A+B\rightarrow AB$ will be second order and the reaction $A+B\rightarrow B$ will be first order after times long compared to a transient whose form is given explicitly. More general equations are obtained to permit the treatment of non-random initial distributions, as occur, for example, in the annealing of radiation damage. In such cases the irregular transients may account for a major portion of the reaction.

I. INTRODUCTION

THE major factors determining the rate of a bimolecular chemical reaction are: (1) the probability that the reactant particles will encounter one another in their random movements and (2) the probability that the energy and steric factors will be appropriate for reaction at the instant of encounter. It often occurs in solid solutions and solutions of viscous fluids that the reactant particles must move from site to site many times before reaching one of their reactant counterparts and that the activation energy for this motion is comparable in magnitude to the activation energy for reaction. When this situation prevails, the rate of reaction is dominated by the first factor above and the reaction process may be described, for the purpose of kinetics, as the diffusion together of the reacting particles.

Several attempts to solve the problem of the diffusion-limited reaction $A+B\rightarrow AB$ have been made in the past.[1–3] In all of these treatments, however, a large degree of independence in the distributions of the reacting particles has been assumed. Consequently, the correlation between the distributions of the A's and the B's due to the reaction process and the effects of this correlation on the reaction rates have not been thoroughly understood. The treatment of this problem is complicated by the fact that many A's compete for each of the B's (and vice versa) and that one or both of the particles are removed from the population upon reaction. These problems have been treated here by dealing directly with the joint probability distributions for each of the AB pairs (every A taken with every B). Higher order probability distributions (ABB triplets, etc.), when required, have been approximated by the superposition technique. That is, one assumes that the correlation between the distributions of the individual particles arises from the independent interaction of each pair of particles. The differential equation for the alteration of the joint distribution of each of the pairs has been derived.[4] These differential equations may be solved for a wide variety of boundary conditions. Consequently, a fairly general and complete mathematical description of the diffusion-limited bimolecular reaction is possible. In particular, it is found that, for a random initial distribution of the particles, the rate of reaction at any time is just the probable rate at which a single A and a single B diffuse together (with an appropriate boundary condition for reaction on close approach) multiplied by the number of A's and the number of B's present at that time. This has been assumed in the past without proof.[1]

It is believed that the equations derived here have considerable practical application in treating experimental data. Section II deals with the definitions. Sections III, IV, and V reduce the kinetics problem to a set of differential equations. Section VI deals with the boundary conditions for the differential equation. Sections VII and VIII formulate the general problem as a boundary value problem. The simplest and most common solutions are given [Eqs. (47)–(50), (55)–(58)]. Section IX summarizes some of the conclusions and gives a few remarks on the practical applications of the theory. The following article in this journal illustrates the technique by an application of the theory to the annealing of radiation damage in solids.

II. DEFINITION OF THE PROBABILITY DENSITIES

In order to avoid mathematical complexities, it will be convenient to restrict the treatment to those cases in which the distributions of the A's and the B's depend only on the distance of each A from each B (and vice versa). The probability distributions will be assumed to be otherwise uniform over the entire medium (i.e., random distributions). As a consequence of their

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[1] M. V. Smoluchowski, Z. physik. Chem. **92**, 192 (1917).

[2] F. Collins and G. Kimball, J. Colloid Sci. **4**, 425 (1949).

[3] H. L. Frisch and F. Collins, J. Chem. Phys. **21**, 2158 (1953).

[4] Differential equations similar to those derived here have also been derived recently by Monchick using a different technique but the same approximation. Monchick, Magee, and Samuel, J. Chem. Phys. **26**, 935 (1957).

interdependence, it will be necessary to deal with a number of distinct probability distributions. These will be defined as follows:

$\bar{\rho}_{Ai}(\mathbf{r}_A,t)dV_A/V=$probability that A_i is in the volume element dV_A at $\mathbf{r}_A$, t.

$\rho_{Ai(Bj)}(\mathbf{r}_A,t;\,\mathbf{r}_B)dV_A/V=$probability that A_i is in dV_A at $\mathbf{r}_A$, t given that B_j is at $\mathbf{r}_B$, t.

These probabilities may be related to the macroscopic properties of the systems by noting that the macroscopic density of A particles, C_A, is given by

$$C_A(\mathbf{r}_A,t)=\frac{1}{V}\sum_i^{N_A^0}\bar{\rho}_{Ai}(\mathbf{r}_A,t), \tag{1}$$

where N_A^0 is the number of A particles at $t=0$. Similarly, the average concentration of A's at $\mathbf{r}_A$, t given that B_j is at $\mathbf{r}_B$ can be expressed as a sum of the $\rho_{Ai(Bj)}$'s. Under the assumption that the distributions depend only on the relative positions of the A's and B's, the $\bar{\rho}_{Ai}$'s are independent of position and are functions of time only. On the other hand, the $\rho_{Ai(Bj)}$ are functions of $\mathbf{r}_A$, t and of the given position of the B atom, $\mathbf{r}_B$. The corresponding probability distributions of the B_j's, $\bar{\rho}_{Bj}$ and $\rho_{Bj(Ai)}$ are defined similarly.

By a well-known theorem from probability theory,[5] we may define pair probability distributions:

$$\rho_{ij}=\rho_{Ai(Bj)}\bar{\rho}_{Bj}=\bar{\rho}_{Ai}\rho_{Bj(Ai)}, \tag{2}$$

such that

$\rho_{ij}(\mathbf{r}_A,\mathbf{r}_B,t)dV_AdV_B/V^2=$probability that A_i is in dV_A at $\mathbf{r}_A$, t and that B_j is in dV_B at $\mathbf{r}_B$, t.

This latter probability density is the joint probability distribution for A_i and B_j. The ρ_{ij}'s may also be related to the macroscopic properties of the system. Consider all of the AB pairs in the system, every A taken with every B. The average number of pairs having the A in dV_A at $\mathbf{r}_A$, t and the B in dV_B at $\mathbf{r}_B$, t is given by

$$C_{AB}(\mathbf{r}_A,\mathbf{r}_B,t)dV_AdV_B=\frac{1}{V^2}\sum_i^{N_A^0}\sum_j^{N_B^0}\rho_{ij}(\mathbf{r}_A,\mathbf{r}_B,t)dV_AdV_B. \tag{3}$$

The purpose of this paper is to show how the ρ_{ij}'s vary with $\mathbf{r}_A$, $\mathbf{r}_B$ and t due to the diffusion and reaction of the A's and B's. This in turn will determine the rate of the diffusion controlled reaction, since this rate depends on the number of pairs having the appropriate AB separation for reaction.

III. CHANGE OF THE JOINT PROBABILITY DENSITIES DUE TO DIFFUSION

Consider the six-dimensional hyperspace formed by the combination of the Cartesian laboratory coordinates of A_i and the Cartesian laboratory coordinates of B_j. This is the space in which ρ_{ij}, the joint probability density, is properly defined. One desires to find the rate of change of ρ_{ij} in the hypervolume element dV_AdV_B. This rate, $\partial\rho_{ij}/\partial t$, is just the change due to the probable flux of A_i and B_j into dV_AdV_B through the hyperfaces of dV_AdV_B plus the change due to the probable rate of destruction of A_i and B_j within dV_AdV_B.

By summing the change in ρ_{ij} due to the flux of particles through each of the twelve hyperfaces of dV_AdV_B, one obtains

$$-[\nabla_A(\mathbf{v}_A\rho_{Ai(Bj)}\bar{\rho}_{Bj})+\nabla_B(\mathbf{v}_B\rho_{Bj(Ai)}\bar{\rho}_{Ai})], \tag{4}$$

where ∇_A is the divergence with respect to the coordinates of A_i and $\mathbf{v}_A$ is the probable vector velocity of A_i at $\mathbf{r}_A$ given that B_j is at $\mathbf{r}_B$. The definitions of ∇_B and $\mathbf{v}_B$ are similar. If one further defines $(\partial\rho_{ij}/\partial t)_{\text{chem}}$ as the probable rate at which ρ_{ij} changes due to the reaction of A_i or B_j in dV_AdV_B, one obtains

$$\partial\rho/\partial t=(\partial\rho/\partial t)_{\text{chem}}-[\nabla_A(\mathbf{v}_A\rho_{ij})+\nabla_B(\mathbf{v}_B\rho_{ij})]. \tag{5}$$

It should be noted that this differential equation applies only to that region where $|\mathbf{r}_A-\mathbf{r}_B|>r_0$, where r_0 is some AB separation within which A and B react.

The probable velocity of an A particle at $\mathbf{r}_A$ given that there is a B particle at $\mathbf{r}_B$ is well known from the theory of stochastic processes.[6] If we restrict ourselves to particles exerting only short-range chemical forces, so that the potential of an unreacted particle is independent of position, this velocity is

$$\mathbf{v}_A=-D_A\nabla_A\ln\rho_{Ai(Bj)}, \tag{6}$$

where D_A is the diffusion coefficient of the A's. Particles with known interaction potentials, e.g., ions, can be treated by including a force term in (6); however, the mathematics become correspondingly more difficult. For simplicity one also assumes that D_A is independent of position. Substituting (6) and the corresponding expression for $\mathbf{v}_B$ into (5), one obtains

$$D_A\nabla_A^2\rho_{ij}+D_B\nabla_B^2\rho_{ij}+(\partial\rho_{ij}/\partial t)_{\text{chem}}=\partial\rho_{ij}/\partial t. \tag{7}$$

It should be noted that Eq. (6) and therefore all subsequent equations have been derived on the assumption[6] that ρ_{ij} does not vary appreciably within distances comparable to the random-flight jump distance. This poses one of the most serious limitations on the theory developed here.

IV. CHANGE OF THE PROBABILITY DENSITY CAUSED BY REACTION

A. Diffusion-Controlled Reaction

One desires to determine the rate of change of ρ_{ij} in dV_AdV_B caused by the reaction of A_i or B_j. Noting that the pair A_iB_j is destroyed if either A_i or B_j react with any other B or A and that A_i or B_j cannot react

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[5] W. Feller, *Probability Theory* (John Wiley and Sons, Inc., New York, 1950), p. 78.

[6] S. Chandrasekar, Revs. Modern Phys. **15**, 1 (1943).

with each other in the region in which Eq. (7) applies ($|\mathbf{r}_A-\mathbf{r}_B|>r_0$), one concludes that

$-(\partial\rho_{ij}/\partial t)_{\text{chem}}dtdV_AdV_B/V^2$
= probability that simultaneously A_i is in dV_A at $\mathbf{r}_A$, t and that B_j is in dV_B at $\mathbf{r}_B$, t and that either A_i reacts with B_k $(k\neq j)$ or B_j reacts with A_m $(m\neq i)$, during the interval dt.

Since the possibilities of reaction of A_i with each of the B_k are mutually exclusive, we may sum the contributions to the above probability due to the reaction of A_i with each of the B_k $(k\neq j)$. The same is true for the reaction of B_j with the A_m $(m\neq i)$. The possibility of both A_i reacting with B_k $(k\neq j)$ and B_j reacting with A_m $(m\neq i)$ simultaneously is not excluded, however, so that a summation of the probabilities for each of the possible reactions is legitimate only if the probability of both particles reacting is negligible with respect to the probability of one reacting. This can be achieved by making dt, dV_A, or dV_B arbitrarily small. One can proceed, therefore, to determine the probabilities of the individual reactions and sum them.

The probability that A_i is in dV_A, B_j is in dV_B, and that A_i reacts with a particular B_k during dt may be expressed as a product of probabilities. It is just the probability that B_j is in dV_B at $\mathbf{r}_B$ given that A_i and B_k are reacting in a small volume element at $\mathbf{r}_A$, times the probability that A_i and B_k react irrespective of where B_j is located. The first of these is a conditional triplet probability. It may be approximated by a superposition technique in which one assumes that the correlation between the particles arises owing to the independent interaction of each of the pairs. Since two B particles interact only by volume exclusion and indirectly by their mutual correlation with the A's, one would expect the direct chemical interaction of A_i with the B's to dominate the required triplet probability. One may therefore approximate the probability that B_j is in dV_B at $\mathbf{r}_B$ given that A_i and B_k are in a small volume element at $\mathbf{r}_A$ by $\rho_{Bj(Ai)}dV_B/V$ or $(\rho_{ij}/\bar{\rho}_{Ai})dV_B/V$. Therefore the required probability is

$$-\frac{\rho_{ij}}{\bar{\rho}_{Ai}}\frac{dV_B}{V}\left[\frac{d\bar{\rho}_{Ai}}{dt}\right]_{Bk}dt\frac{dV_A}{V},\tag{8}$$

where $-[d\bar{\rho}_{Ai}/dt]_{Bk}dtdV_A/V$ is the probability that A_i and B_k react in dV_A during dt irrespective of where B_j is located. Summing these probabilities for the reaction of A_i with all B_k $(k\neq j)$ and the probabilities for reaction of B_j with all A_m $(m\neq i)$, one obtains

$$(\partial\rho_{ij}/\partial t)_{\text{chem}}=f_{ij}(t)\rho_{ij},\tag{9}$$

where

$$f_{ij}(t)=\frac{1}{\bar{\rho}_{Ai}}\sum_{k\neq j}^{N_B^0}\left[\frac{d\bar{\rho}_{Ai}}{dt}\right]_{Bk}+\frac{1}{\bar{\rho}_{Bj}}\sum_{m\neq i}^{N_A^0}\left[\frac{d\bar{\rho}_{Bj}}{dt}\right]_{Am}.\tag{10}$$

Substitution of (9) into Eq. (7) yields

$$D_A\nabla_A^2\rho_{ij}+D_B\nabla_B^2\rho_{ij}+f_{ij}(t)\rho_{ij}=\partial\rho_{ij}/\partial t.\tag{11}$$

It may be noted that $f_{ij}(t)$ is never positive.

If (11) can be solved for ρ_{ij}, one can immediately determine the probable rate of the reaction $A_i+B_j\to AB$. It is merely the flux of A_i into B_j or vice versa. This flux is given by[7]

$$\left[\frac{d\bar{\rho}_{Ai}}{dt}\right]_{Bj}=\left[\frac{d\bar{\rho}_{Bj}}{dt}\right]_{Ai}=\frac{-4\pi r_0^2(D_A+D_B)}{V}\left[\frac{\partial\rho_{ij}}{\partial r}\right]_{r0},\tag{12}$$

where $r=|\mathbf{r}_A-\mathbf{r}_B|$ and r_0 is an AB separation outside of which the AB interaction is independent of r, but inside of which the interaction potential rapidly increases to its value for the AB bond. The total rate of the reaction $A+B\to AB$ is given by

$$\frac{dC_A}{dt}=\frac{dC_B}{dt}=\frac{1}{V}\sum_i^{N_A^0}\sum_j^{N_B^0}\left[\frac{d\rho_{Ai}}{dt}\right]_{Bj}$$

$$=-\frac{4\pi r_0^2(D_A+D_B)}{V^2}\sum_i\sum_j\left[\frac{\partial\rho_{ij}}{\partial r}\right]_{r0}.\tag{13}$$

This result may be modified to account for the reaction $A+B\to B$, simply by allowing $[\partial\rho_{Bi}/dt]_{Aj}$ and dC_B/dt to equal zero rather than the values given by (12) and (13).

B. Sinks and Sources Due to Other Reactions

Sometimes in physical situations in which diffusion-limited reactions occur, other reactions which alter the concentration of the reactants will occur simultaneously. It is often possible to describe these phenomena mathematically and to include their effects in the differential equations for the rates of change of the probability densities. However, no attempt will be made to include general sink terms in the present treatment. It is simply noted that the inclusion of specific sink terms in the formulation is not impossible, but the resulting mathematics problems become somewhat more formidable.

V. DIFFERENTIAL EQUATION FOR THE JOINT PROBABILITY DENSITY

The $N_A^0N_B^0$ equations of the form (11) are the differential equations for the pair distribution functions. In their present form they are not particularly amenable to solution. However, a number of simplifications are possible. These simplifications are presented below with a discussion of the general procedure for solving the equations.

Since the cases of interest are those in which the distribution of A's and B's depend only on the relative

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[7] If Eq. (12) is not self-evident it may be obtained by using Green's theorem to integrate Eq. (16) once over the entire volume and considering the significance of the individual terms.

positions of the A's and B's, it will be convenient to transform the variables in Eq. (11) as follows:

$$\begin{aligned} x_1&=\frac{D_Bx_A+D_Ax_B}{D_A+D_B}, & x_2&=x_A-x_B,\\ y_1&=\frac{D_By_A+D_Ay_B}{D_A+D_B}, & y_2&=y_A-y_B,\\ z_1&=\frac{D_Bz_A+D_Az_B}{D_A+D_B}, & z_2&=z_A-z_B. \end{aligned} \tag{14}$$

Because of the importance of this new coordinate system, it will be convenient to deal with an infinite medium only. Use of a finite medium causes the limits of the variable x_2 to depend on the value of x_1, etc. Use of an infinite medium need not limit the applicability of the results, since nearly all laboratory experiments involve dimensions which are essentially infinite with respect to atomic dimensions. This will not be the case, of course, if the flux of particles to the surface of the sample is an important matter.

Substituting the new variables of (14) into Eq. (11), one obtains

$$\frac{D_AD_B}{D_A+D_B}\nabla_1^2\rho_{ij}+(D_A+D_B)\nabla_2^2\rho_{ij}+f_{ij}(t)\rho_{ij}=\frac{\partial\rho_{ij}}{\partial t}. \tag{15}$$

Since ρ_{ij} is independent of x_1, y_1, and z_1, it follows that $\nabla_1^2\rho_{ij}=0$. If one further transforms x_2, y_2, and z_2 into spherical coordinates and assumes no angular dependence, Eq. (15) takes the form

$$D\left[\frac{\partial^2\rho_{ij}}{\partial r^2}+\frac{2}{r}\frac{\partial\rho_{ij}}{\partial r}\right]+f_{ij}(t)\rho_{ij}=\frac{\partial\rho_{ij}}{\partial t}, \tag{16}$$

where

$$D=D_A+D_B. \tag{17}$$

The $N_A^0N_B^0$ differential equations of the form (16) are coupled through the functions $f_{ij}(t)$. This coupling may be simplified by the substitution

$$\rho_{ij}=\frac{w_{ij}}{r}\exp\left[\int_0^t f_{ij}dt\right]. \tag{18}$$

The differential equations for the w_{ij} are no longer coupled and become

$$D\frac{\partial^2 w_{ij}}{\partial r^2}=\frac{\partial w_{ij}}{\partial t}. \tag{19}$$

The problem, therefore, centers around the solution of the equations of the form (19) with the appropriate boundary conditions. At first sight, it might seem that, even if (19) were solved, for each of the w_{ij}, Eq. (18) could not be solved for the ρ_{ij}, since the f_{ij} depend on the ρ_{ij} in a complicated manner. This problem is greatly simplified, however, if one takes advantage of a few facts demanded by the physical situation.

One notes that the differential equations for the ρ_{ij} are all identical. One expects, therefore that all of the ρ_{ij} will be the same unless special boundary conditions exist for certain of the pairs. It will become apparent in the next section that these boundary conditions can be different only if the initial knowledge of the various A_iB_j pairs is different. If all of the particles are initially randomly distributed with respect to one another, all of the ρ_{ij} are identical and the treatment is quite straightforward. In general there will be at most only a very few types of the ρ_{ij}. In the remainder of this paper we shall deal in detail with the case for which all of the ρ_{ij} are identical. More general cases may be handled, however, as will be shown in the following paper in this journal.

Another factor which simplifies the solution of (18) and permits the evaluation of the f_{ij} is that C_{AB}, the sum of the ρ_{ij} [see Eq. (3)] must become independent of r for large values of r. Since the system is infinite, this limiting value, $C_{AB}(\infty,t)$, is just the average value over the system. We have, therefore,

$$\begin{aligned} C_AC_B&=C_{AB}(\infty,t)\\ &=\frac{1}{V^2}\sum_i^{N_A^0}\sum_j^{N_B^0}\exp\left(\int_0^t f_{ij}dt\right)U_{ij}(\infty,t), \end{aligned}\tag{20}$$

where

$$U_{ij}(r,t)=w_{ij}(r,t)/r. \tag{21}$$

This single equation resulting from the boundary condition on the ρ_{ij} at large values of r will go a long way toward the determination of the f_{ij}. If all of the ρ_{ij} are identical, equation (20) completely determines f_{ij}. In this case, (20) becomes

$$C_AC_B=C_A^0C_B^0U_{ij}(\infty,t)\exp\left[\int_0^t f_{ij}dt\right], \tag{22}$$

where

$$C_A^0=N_A^0/V,\quad C_B^0=N_B^0/V. \tag{23}$$

Elimination of f_{ij} from Eqs. (18) and (22) leads to

$$\rho_{ij}=\frac{C_AC_B}{C_A^0C_B^0U_{ij}(\infty,t)}U_{ij}(r,t). \tag{24}$$

The effect of the coupling due to competition is then simply to supplement the boundary condition at time $t=0$ by a stronger condition requiring ρ_{ij} to approach $C_AC_B/C_A^0C_B^0$ at large values of r at all times. One may evaluate C_A and C_B by integrating Eq. (13) which takes the form

$$\frac{dC_A}{dt}=\frac{dC_B}{dt}=-4\pi r_0^2DC_A^0C_B^0\left[\frac{\partial\rho_{ij}}{\partial r}\right]_{r_0}. \tag{25}$$

Taking the derivative of (24) and substituting into (25), one obtains

$$\frac{dC_A}{dt}=\frac{dC_B}{dt}=-4\pi r_0^2 D\frac{C_A C_B}{U_{ij}(\infty,t)}\left[\frac{\partial U_{ij}(r,t)}{\partial r}\right]_{r0}, \quad (26)$$

which can be integrated by taking advantage of

$$C_B=C_B^0-[C_A^0-C_A]. \quad (27)$$

One may, therefore, readily obtain C_A, C_B, and C_{AB} from Eqs. (24), (26), and (27), if Eq. (19) can be solved for w_{ij}. It should be noted that Eqs. (22) through (27) were derived on the assumption that all of the ρ_{ij} were identical. The situation will be slightly more complex, if the initial knowledge of all of the pairs is not the same. However, the technique will be similar. Such a case is treated in the following paper on radiation damage in solids.

VI. BOUNDARY CONDITIONS

In order to solve the differential equations for the joint probability distribution, three boundary conditions are required. These will be determined from the physical situation as follows:

1. $\rho_{ij}\rightarrow\rho_{\text{eq}}$ as $t\rightarrow\infty$, where ρ_{eq} is the equilibrium probability density determined from the equilibrium concentrations of A's and B's.
2. $\rho_{ij}=g(r)$ when $t=0$, which is determined from the initial distribution of each A_i with respect to each B_j (or vice versa).
3. A boundary condition at some small AB separation, r_0, which adequately describes the mechanism of reaction of an A and a B and their subsequent removal from the population of A's and B's.

The first boundary condition must be determined from each experimental situation. It will not in general, greatly complicate the mathematical problem involved, for it can always be reduced to the boundary condition $\rho_{ij}^*=0$ by the substitution $\rho_{ij}^*=\rho_{ij}-\rho_{\text{eq}}$. The second boundary condition must also be specified for each particular case. By far the simplest case mathematically, and probably the most common, is a random initial distribution of the A's with respect to the B's. This leads to the boundary condition $\rho_{ij}=1$ when $t=0$. More complex initial distributions can be dealt with, however, and sometimes occur as is illustrated in the following paper. The third boundary condition above is by far the most difficult to formulate. In order to avoid unwieldly complications in the mathematics, it is necessary to oversimplify the problem grossly. Some of the more acceptable formulations of this boundary condition are discussed below.

If one assumes that the irreversible combination of an A and a B occurs when they approach one another to within a distance r_0, but that no chemical interaction occurs when their separation exceeds r_0, one is led to the following boundary condition on ρ_{ij}:

$$\rho_{ij}=0 \quad \text{for} \quad r\leqq r_0. \quad (28)$$

This boundary condition was first proposed by Smoluchowski.[1] It is not so unrealistic as it might at first seem. It implies that the force between an A and a B follows a step function with the step occurring at r_0. This is in fair accord with the strong, short-range forces of a chemical bond. If one desires to account for the reversibility of the reaction, a fair approximation is to require that

$$\rho_{ij}=\rho_{\text{eq}} \quad \text{for} \quad r\leqq r_0. \quad (29)$$

This can be simplified to the previous case by the substitution $\rho_{ij}^*=\rho_{ij}-\rho_{\text{eq}}$.

The major objection to the Smoluchowski boundary condition, outside of its idealization of the AB interaction potential, is that it cannot account for the possibility of reflection upon collision of an A and a B. If, as suggested in the introduction, the reaction rate is determined in part by the energy and steric factors at the instant of collision, a more elaborate boundary condition at r_0 will be required. Collins[2] has suggested that we may define a pair separation, $r_0-\Delta r_0$ to r_0, within which the rate of reaction is no longer diffusion controlled, but proceeds according to first-order chemical kinetics. He suggests that the probable rate of reaction of A_i and B_j be given by

$$\left[\frac{d\bar{p}_{Ai}}{dt}\right]_{Bj}=\left[\frac{d\bar{p}_{Bj}}{dt}\right]_{Ai}=k(4\pi r_0^2\Delta r_0)\frac{\rho_{ij}(r_0,t)}{V}, \quad (30)$$

where k is a chemical rate constant. Since this rate of reaction must also be equal to the flux through the sphere of radius r_0, we have

$$\left[\frac{\partial\rho_{ij}}{\partial r}\right]_{r_0,t}=\beta\rho_{ij}(r_0,t), \quad (31)$$

where

$$\beta=k\Delta r_0/D. \quad (32)$$

This boundary condition will be referred to as the radiation boundary condition since it accounts for the "reflection" of the particles on collision and since the resulting boundary value problem is quite similar to the radiation problem in heat flow theory.

A further modification of this boundary condition may be necessary for the reaction $A+B\rightarrow B$. This is due to the growth of the B particle as in the growth of colloids and in precipitation from solid solution. Here either the Smoluchowski or radiation boundary condition may be used, but the value of r_0 will vary with time depending on the rate of reaction.

VII. SOLUTION FOR THE SMOLUCHOWSKI BOUNDARY CONDITION

A. General Solution

The mathematical formulation of the problem may be made by summarizing our previous conclusions as follows:

$$C_{AB}(r,t)=\frac{1}{V^2}\sum_i^{N_A{}^0}\sum_j^{N_B{}^0}\rho_{ij}(r,t), \qquad \text{[from (3)]} \quad (33)$$

$$\frac{dC_A}{dt}=\frac{dC_B}{dt}=-\frac{4\pi r_0{}^2D}{V^2}\sum_j^{N_A{}^0}\sum_i^{N_B{}^0}\left[\frac{\partial\rho_{ij}}{\partial r}\right]_{r0}, \qquad \text{[from (13) and (17)]} \quad (34)$$

$$C_B=C_B{}^0-[C_A{}^0-C_A], \qquad \text{[from (27)]} \quad (35)$$

$$\rho_{ij}=\frac{w_{ij}}{r}\exp\left(\int_0^t f_{ij}dt\right), \qquad \text{[from (18)]} \quad (36)$$

$$f_{ij}=\frac{C_A{}^0}{C_A}\sum_{k\neq j}^{N_B{}^0}\frac{-4\pi r_0{}^2D}{V}\left[\frac{\partial\rho_{ik}}{\partial r}\right]_{r0}+\frac{C_B{}^0}{C_B}\sum_{m\neq i}^{N_A{}^0}\frac{-4\pi r_0{}^2D}{V}\left[\frac{\partial\rho_{mj}}{\partial r}\right]_{r0}, \qquad \text{[from (10) and (12)]} \quad (37)$$

$$D\partial^2w_{ij}/\partial x^2=\partial w_{ij}/\partial t, \quad x=r-r_0. \qquad \text{[from (19)]} \quad (38)$$

The boundary conditions on the ρ_{ij} are

$$\begin{gathered}\rho_{ij}\to 0 \quad \text{as} \quad t\to\infty,\\ \rho_{ij}(r,\, t=0)=h(r) \quad \text{for} \quad r>r_0,\\ \rho_{ij}(r=r_0,\, t)=0.\end{gathered} \qquad (39)$$

The corresponding boundary conditions on w are

$$\begin{gathered}w_{ij}\to 0 \quad \text{as} \quad t\to\infty,\\ w_{ij}(x,\, t=0)=(x+r_0)h(x+r_0)=g(x) \quad \text{for} \quad x>0,\\ w_{ij}(x=0,\, t)=0.\end{gathered} \qquad (40)$$

The general solution of (38) with the boundary condition (40) is well-known from the theory of heat flow[8] and is

$$w_{ij}(x,t)=\frac{1}{\sqrt{\pi}}\int_{-x/2(Dt)^{\frac{1}{2}}}^{\infty}g(x+2(Dt)^{\frac{1}{2}}\alpha)\exp(-\alpha^2)d\alpha-\frac{1}{\sqrt{\pi}}\int_{x/2(Dt)^{\frac{1}{2}}}^{\infty}g(-x+2(Dt)^{\frac{1}{2}}\alpha)\exp(-\alpha^2)d\alpha. \quad (41)$$

The general solution of the above set of equations is difficult because of the set of coupled integral equations (36) and (37). But as remarked earlier, these equations may often be reduced to a few algebraic equations by virtue of additional knowledge of the physical situation. For example, when all of the ρ_{ij} are identical, we replace Eqs. (33), (34), (36), and (37) by the following:

$$C_{AB}(r,t)=\frac{C_AC_B}{U_{ij}(\infty,t)}U_{ij}(r,t), \qquad (42)$$

$$U_{ij}(r,t)=\frac{w_{ij}(r,t)}{r}, \qquad \text{[from (21)]} \quad (43)$$

$$\frac{dC_A}{dt}=\frac{dC_B}{dt}=-\frac{4\pi r_0{}^2C_AC_B}{U_{ij}(\infty,t)}\left[\frac{\partial U_{ij}(r,t)}{\partial r}\right]_{r0}. \qquad \text{[from (26)]} \quad (44)$$

The simultaneous solution of (35), (41), (42), (43), and (44) is elementary. We have, therefore, a complete solution to the diffusion-controlled reaction, if all of the ρ_{ij} are identical and the Smoluchowski boundary condition is valid.

B. Detailed Solution for the Uniform Initial Distribution

Consider the problem outlined in the previous section when the initial distribution of A's with respect to the B's at time $t=0$ is uniform. That is, $\rho_{ij}(r,\, t=0)=1$ for all ρ_{ij}. In this case, all of the ρ_{ij} are identical. The initial boundary condition on w_{ij} is

$$w_{ij}(x,0)=(x+r_0). \qquad (45)$$

In this case, (42) takes the form

$$C_{AB}=C_AC_B\left(1-\frac{2r_0}{r}\int_{(r-r_0)/2(Dt)^{\frac{1}{2}}}^{\infty}\frac{\exp(-\alpha^2)}{\sqrt{\pi}}d\alpha\right), \qquad (46)$$

and (44) becomes

$$\frac{dC_A}{dt}=\frac{dC_B}{dt}=-\kappa\left[1+\frac{r_0}{(\pi Dt)^{\frac{1}{2}}}\right]C_AC_B, \qquad (47)$$

where

$$\kappa=4\pi r_0(D_A+D_B). \qquad (48)$$

One may readily integrate (45) by taking advantage of (35). The result, for the case in which $C_A{}^0=C_B{}^0$, is

$$\frac{1}{C_A}=\frac{1}{C_B}=\frac{1}{C_A{}^0}+\kappa\left[1+\frac{2r_0}{(\pi Dt)^{\frac{1}{2}}}\right]t. \qquad (49)$$

For the case in which $C_A{}^0\neq C_B{}^0$, the result is

$$C_A=\frac{(C_A{}^0-C_B{}^0)C_A{}^0}{C_A{}^0-C_B{}^0\exp\left\{-\kappa(C_A{}^0-C_B{}^0)\left[1+\frac{2r_0}{(\pi Dt)^{\frac{1}{2}}}\right]t\right\}}, \qquad (50A)$$

$$C_B=\frac{(C_B{}^0-C_A{}^0)C_B{}^0}{C_B{}^0-C_A{}^0\exp\left\{-\kappa(C_B{}^0-C_A{}^0)\left[1+\frac{2r_0}{(\pi Dt)^{\frac{1}{2}}}\right]t\right\}}. \qquad (50B)$$

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[8] R. Churchill, *Fourier Series and Boundary Value Problems* (McGraw-Hill Book Company, Inc., New York, 1941), p. 120.

Substitution of (49) or (50) into (46) gives C_{AB}, the density of AB pairs, as a function of r and t. Both (49) and (50) reduce to second-order kinetics for times long compared to r_0^2/D. If either C_A or C_B is much greater than the other, Eq. (50) will reduce to a first-order kinetics.

The above solutions may be modified readily to account for the reaction $A+B\rightarrow B$, such as occurs in the growth of colloids. In this case, C_B is constant and equal to $C_B{}^0$. This reaction follows first-order kinetics after times long compared with r_0^2/D.

The joint AB probability density as a function of the AB separation after various times is shown in Fig. 1 for the case in which $C_A{}^0=C_B{}^0$ [Eqs. (46) and (49)]. It should be noted that the rapid depletion of AB pairs with separations of a few r_0 is a direct consequence of the assumed diffusion-limited mechanism.

A consideration of the above reaction at times of the order of r_0^2/D shows that the apparent second-order (or first-order) rate constant is time-dependent and becomes very large as t approaches zero. It appears that the transients will be longest for particles which diffuse slowly and have a large capture radius. However, the ratio of the length of the transient period, r_0^2/D, to the mean life of the A's, τ_A, is a better measure of the significance of the transient. An order of magnitude approximation for this ratio is given by

$$\frac{r_0^2/D}{\tau_A}\approx\tfrac{4}{3}\pi r_0{}^3C_B{}^0. \tag{51}$$

This approximation is valid for both $A+B\rightarrow AB$ and $A+B\rightarrow B$. It should be noted, however, that this transient is a consequence of the assumed boundary conditions. The postulated uniform initial distribution existing right up to the capture radius r_0 caused an infinite initial gradient in ρ. This is, of course, impossible experimentally so that the very early stages of the transient will never be observed. Furthermore, the validity of Fick's law in the region of the large gradient is not at all certain. The objection applies, however, only at the very earliest time so that the form of the transient given above should be at least qualitatively correct. Collins[2] has suggested that Fick's law will be a more valid approximation if the radiation boundary condition is used. This is undoubtedly true since the postulated infinite initial gradient can be achieved only if there is a barrier to reaction upon collision. Further, the large gradient in the ρ_{ij} existing at the barrier is no longer in the region to which Fick's law is applied. This modified boundary condition is treated in the following section.

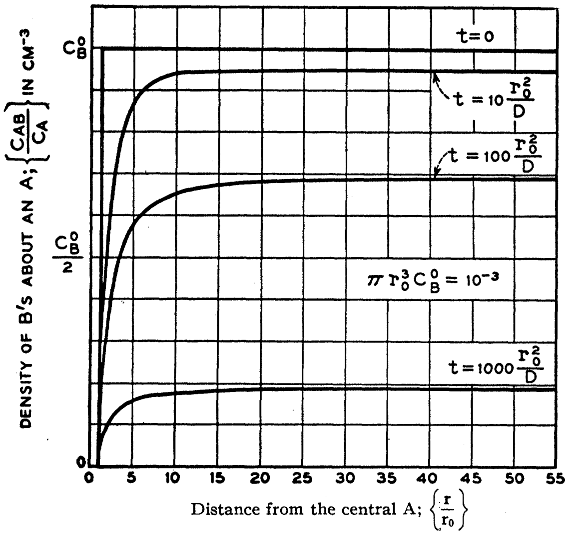

FIG. 1. Probable distribution of B's about a central A particle after various times for a diffusion-limited bimolecular reaction.

VIII. SOLUTION FOR THE RADIATION BOUNDARY CONDITION

The radiation boundary condition requires that:

$$\left[\frac{\partial\rho_{ij}}{\partial r}\right]_{r_0,t}=\beta\rho_{ij}(r_0,t).\quad\text{[from (31)]} \tag{52}$$

The mathematical formulation of the problem is identical with that for the Smoluchowski boundary condition (Sec. VIIA) except that (40), the boundary conditions on w, become

$$\begin{aligned} &w_{ij}\rightarrow 0 \quad\text{as}\quad t\rightarrow\infty,\\ &w_{ij}(x,t=0)=g_{ij}(x), \end{aligned} \tag{53}$$

$$\left[\frac{\partial w_{ij}}{\partial x}\right]_{0,t}=\left(\beta+\frac{1}{r_0}\right)w_{ij}(0,t).$$

The boundary value problem is familiar in heat-flow theory as the radiation boundary condition for a semi-infinite solid.[9] The problem is simplified to that of the Smoluchowski boundary condition by the substitution

$$v_{ij}=w_{ij}-\left(\frac{1}{\beta+1/r_0}\right)\frac{\partial w_{ij}}{\partial x}. \tag{54}$$

After a solution is obtained for v_{ij}, however, (54) must be integrated. This is not in general difficult so that it is possible to obtain solution for the w_{ij} for any simple initial distribution of the A's with respect to the B's. For a uniform initial distribution of the A's with respect to the B's, all of the ρ_{ij} are identical and the

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[9] H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids* (Clarendon Press, Oxford, 1947).

reaction rate is given by

$$\frac{dC_A}{dt}=-4\pi r_0{}^2DC_AC_B\left\{\beta-\frac{r_0\beta^2}{r_0\beta+1}\right.$$
$$\left.\times\left[1-2e^{mt}\int_{(mt)^{\frac{1}{2}}}^{\infty}\frac{\exp(-\alpha^2)}{\sqrt{\pi}}d\alpha\right]\right\}, \tag{55}$$

where

$$m=D\left(\frac{r_0\beta+1}{r_0}\right)^2. \tag{56}$$

For very short times such that $mt\cong 0$, the rate is

$$dC_A/dt=-4\pi r_0{}^2\Delta r_0kC_AC_B. \tag{57}$$

For very long times, such that $mt\rightarrow\infty$, the rate is

$$\frac{dC_A}{dt}=-4\pi r_0{}^2D\left(\frac{\beta}{r_0\beta+1}\right)C_AC_B. \tag{58}$$

Both of these rates are simple second-order rates. However, the rate constants are different unless $r_0\beta\ll 1$, in which case the reaction is not diffusion-limited. Consequently a transition period will exist in a naive chemical-kinetics treatment of a truly diffusion-limited reaction.

One may consider how the form of the rate equation, (55), varies with β. When $r_0\beta\ll 1$, the rate (55) takes the form (57) and the reaction follows simple second-order kinetics, i.e., the reaction is not diffusion-controlled. When $r_0\beta\gg 1$, the rate becomes identical with (47), the rate when the Smoluchowski boundary condition is valid. This is to be expected since the radiation boundary condition becomes the Smoluchowski boundary condition as β approaches infinity.

Because of the increased complexity of the equations, the treatment of experimental data assuming the radiation boundary condition would require more effort than would be required if the Smoluchowski boundary condition were assumed. However, a better fit of the data should be obtained with the radiation boundary condition since it is more general. Therefore the radiation boundary condition should be applied to cases in which a definite activation energy for reaction upon collision is expected.

IX. CONCLUSIONS AND CONSIDERATION OF APPLICATIONS

Physical situations in which diffusion-controlled reactions occur are well known. They occur, for example, in the growth of colloids, the quenching of fluorescence, chemical reactions in solids, and annealing of defects in solids. Approximate descriptions of the diffusion process and even the assumption of simple second-order kinetics have often been used with moderate success in the treatment of data obtained in such experiments. The present treatment shows the conditions in which these approximations are expected to be valid, and offers an explanation of the transients observed. A valid interpretation of the experimental parameters is possible.

The problem of the diffusion-limited bimolecular reaction has been formulated in terms of the joint probability densities of the pairs of reacting particles. The formulation leads to differential equations which may be solved for a variety of boundary conditions. The problem has been solved in detail for a random initial distribution of the reacting particles. It is found that the rate of reaction at any time is just the expected rate at which a single A and a single B diffuse together (with an appropriate boundary condition for reaction on close approach) multiplied by the number of A's and the number of B's present at that particular time. If the barrier for reaction upon collision is of the same order of magnitude as the barrier for diffusion, the rate of the reaction $A+B\rightarrow AB$ will be of second order and the reaction $A+B\rightarrow B$ will be of first order after times long compared to $r_0{}^2/D$ (or $\frac{4}{3}\pi r_0{}^3C_B{}^0$ mean lives). The rate constants are expressible in terms of the capture radius, r_0, and the diffusion constant, $D=D_A+D_B$. The solution to the kinetics problem may be obtained for other initial distributions, as will be illustrated in the following paper in this journal on the annealing of radiation damage in solids.

ACKNOWLEDGMENTS

The author would like to express his thanks to Howard Reiss for suggesting this problem and for his continued interest and help in its solution. Thanks are also due to H. L. Frisch for helpful discussions and criticism.