Competitive effects in diffusion-controlled reactions*

J. M. Deutch

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

B. U. Felderhof

Institut für Theoretische Physik A, RWTH Aachen, Templergraben 64, 51 Aachen, West Germany

Michael J. Saxton

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

(Received 18 February 1976)

We study diffusion-controlled reactions in a system of static sinks reacting with diffusing molecules and investigate the competitive effects due to the global distribution of sinks. We also study the effect of competition on growth or shrinkage of droplets in coagulation or burning.

I. INTRODUCTION

In a previous article[1] we have investigated the effect of concentration on the rate of diffusion-controlled reactions and have shown that the rate coefficient increases with concentration from its dilute limit value as given by the classical Smoluchowski theory. In a system of static sinks reacting with diffusing molecules, one would expect that the competition for molecules between sinks leads to a decrease of the total rate of reaction. This competition arises due to the geometric distribution of sinks as viewed on a macroscopic scale, whereas the rate coefficient mentioned above measures the rate in a locally uniform region. In this article we explore the competitive effect due to the global distribution of sinks on the basis of the macroscopic diffusion-reaction equation for the average number density of molecules. In Sec. II we describe the model in more detail and in Sec. III we study shape factors for catalytic pellets. In Sec. IV we investigate the effect of competition on the growth or shrinkage of sinks in coagulation or burning. The results of this theory will apply to a diverse range of physical and chemical phenomena which involve diffusive transport as a rate limiting step.

II. THE BASIC MODEL

The basic model we consider is the steady state diffusion of molecules to a random array of $\mathfrak{N}$ spherical sinks contered at $\mathbf{r}_1, \ldots, \mathbf{r}_{\mathfrak{N}}$. To lowest order the microscopic equations for this system are[1]

$$n(\mathbf{r}) = n_0(\mathbf{r}) - \sum_{l=1}^{\mathfrak{N}} \frac{q_l}{|\mathbf{r} - \mathbf{r}_l|} , \qquad (2.1)$$

where $n(\mathbf{r})$ is the steady state concentration of molecules at position $\mathbf{r}$ and q_l is related to the flux into the sink j_l by

$$j_l = 4\pi D_0 q_l , \qquad (2.2)$$

where D_0 is the unperturbed diffusion coefficient in the medium. In Eq. (2.1), $n_0(\mathbf{r})$ is an arbitrary solution of the homogeneous Laplace equation $\nabla^2 n_0 = 0$. Usually this solution will be fixed by specifying the conditions at infinity, e.g., $n_0(r) = n_0 =$ constant. In an electrostatic analogue q_l may be called the "induced charge" of the sink. An immediate extension[1] of the Smoluchowski theory of diffusion-controlled reactions leads to self-consistent equations for determining the q_l:

$$q_l = a\left[n_0(\mathbf{r}_l) - \sum_{m(\neq l)}^{\mathfrak{N}} r_{ml}^{-1} q_m\right] , \qquad (2.3)$$

when the sinks are all perfectly absorbing and of identical radius a; in Eq. (2.3) $r_{ml}^{-1} = |r_m - r_l|^{-1}$. For the more general case where the sinks have different radii, Eq. (2.3) is valid with a replaced by a_l, the radius of the lth sink.

While the principal application is to the case of statistically distributed sinks, it is important to note that for regular arrangements Eq. (2.3) can easily be solved numerically and, in some favorable cases, analytically. For example when $\mathfrak{N}$ sinks of equal radius a are arranged in a regular planar polygon with sides of length L then Eq. (2.3) can be solved by Fourier transform.[2] The total absorption rate for this array is

$$J_{\mathfrak{N}} = 4\pi D_0 a n_0 \mathfrak{N}[1 + (a/L)S(\mathfrak{N})]^{-1} , \qquad (2.4)$$

where

$$S(\mathfrak{N}) = \sin\left(\frac{\pi}{\mathfrak{N}}\right) \sum_{p=1}^{\mathfrak{N}-1} \left[\sin\left(\frac{\pi p}{\mathfrak{N}}\right)\right]^{-1} . \qquad (2.5)$$

Thus in the special case of two sinks, the total absorption rate $J_2(L)$ varies with the sink separation L according to

$$J_2(L) = 2k_e[1 + (a/L)]^{-1} , \qquad (2.6)$$

where $k_e = 4\pi D_0 a\, n_0$ is the Smoluchowski absorption rate for a single sink. Note that the absorption rate $J_{\mathfrak{N}}$ is less than the sum of the rates from isolated sinks. For large $\mathfrak{N}$ the result Eq. (2.4) is[2]

$$J_{\mathfrak{N}}(L) = 4\pi D_0 n_0 L \mathfrak{N} / \ln \mathfrak{N} .$$

When the sinks are statistically distributed the average number density of the molecules $N(\mathbf{r}, t)$ satisfies the macroscopic continuum equation

$$\frac{\partial N}{\partial t} = \nabla \cdot [D(\rho)\nabla N] - k(\rho)\rho N , \qquad (2.7)$$

where $D(\rho)$ is an effective diffusion coefficient in the random medium, $k(\rho)$ is the effective rate coefficient and ρ is the number density of sinks. It has been shown in I that in the mean field approximation, when both the

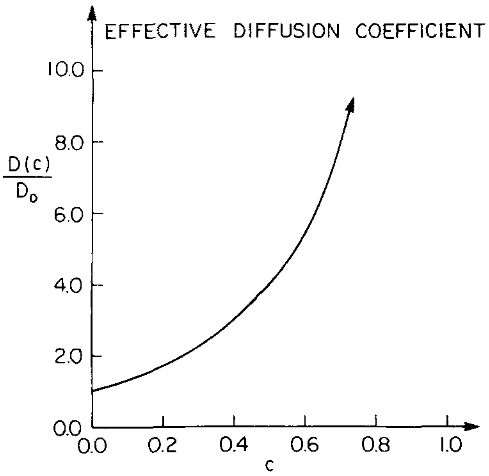

FIG. 1. The ratio of the effective diffusion coefficient to the unperturbed diffusion coefficient $D(c)/D_0$ versus volume fraction c of the perfectly absorbing sinks. In the mean field approximation when induced charges and dipoles are considered this quantity is given by the Claussius–Mossotti function. Eq. (2.10) exhibited above.

effect of included "charges" and "dipoles" is included, one finds for the rate coefficient for completely absorbing sinks

$$k_0 = 4\pi D_0 a \ , \tag{2.8}$$

which is identical with the dilute limit value. When correlations between sinks are taken into account the rate coefficient becomes dependent on ρ. In I we have found the rate coefficient to increase with the density ρ.

For the effective diffusion coefficient one finds in the mean field approximation

$$D(\rho) = D_0 \sigma(\rho) \ , \tag{2.9}$$

where $\sigma(\rho)$ is an acceleration factor given by a Clausius–Mossotti type relation

$$(\sigma - 1)/(\sigma + 2) = \tfrac{4}{3}\pi a^3 \rho \equiv c \ . \tag{2.10}$$

In Fig. 1 the effective diffusion coefficient is plotted versus c, the volume fraction of sinks. Again when correlations between sinks are taken into account this result must be corrected. In this article we shall use a value k for the rate coefficient and a value D for the diffusion coefficient without specifying their density dependence.

III. SOLUTIONS OF THE STEADY-STATE CONTINUUM EQUATION

In the steady state the macroscopic equation becomes, when $k(\rho)$ and $D(\rho)$ are replaced by their dilute limit values,

$$D_0 \nabla^2 N(\mathbf{r}) = k_0 \rho(\mathbf{r}) N(\mathbf{r}) \ . \tag{3.1}$$

We shall be particularly interested in cases where the absorbing sinks are distributed in a region of space V, according to $\rho(\mathbf{r})$. The total steady-state rate of disappearance of molecules into the sinks J_T is given by

$$J_T = k_0 \int_V \rho(\mathbf{r}) N(\mathbf{r})\, d\mathbf{r} \ . \tag{3.2}$$

The differential equation (3.1) may be transformed into the integral equation

$$N(\mathbf{r}) = N_0(\mathbf{r}) - \frac{k_0}{4\pi D_0} \int_V \frac{1}{|\mathbf{r} - \mathbf{r}'|} \rho(\mathbf{r}') N(\mathbf{r}')\, d\mathbf{r}' \ , \tag{3.3}$$

where $N_0(r)$ is an arbitrary solution of the homogeneous Laplace equation $\nabla^2 N_0 = 0$. If we assume that $N_0(r)$ tends to a constant N_0 at infinity one has asymptotically for large r

$$N(\mathbf{r}) = N_0[1 - (l/r)] \ , \tag{3.4}$$

where l is a "scattering length,"

$$l = (k_0/4\pi D_0 N_0) \int \rho(\mathbf{r}') N(\mathbf{r}')\, d\mathbf{r}' \ . \tag{3.5}$$

Accordingly the volume V will absorb molecules at a total rate

$$J_T = 4\pi D_0 N_0 l \ , \tag{3.6}$$

which is equivalent to the classical Smoluchowski result for a sphere of radius l with perfectly absorbing surface. It follows that the total absorption J_T may be determined if the scattering length for zero energy s-wave scattering from a potential $\rho(r)$ can be found. This analogy between quantum mechanical scattering and the solution of classical transport equations arises in approximate theories of frictional properties of dilute polymer solutions.[3]

As a special case we consider a uniform distribution ρ of absorbing sinks within a radius R. For this case we have

$$\begin{aligned} \nabla^2 N(\mathbf{r}) &= \kappa^2 N(\mathbf{r}) \quad \text{for } r \leq R \ , \\ \nabla^2 N(\mathbf{r}) &= 0 \quad \text{for } r > R \ , \end{aligned} \tag{3.7}$$

where the shielding length κ^{-1} is defined by

$$\kappa^2 = k_0 \rho / D_0 = 4\pi a \rho \ . \tag{3.8}$$

The solution of Eq. (3.7), with the condition that $N(r)$ and $N'(r)$ are continuous at $r = R$ and that $N(\mathbf{r})$ tends to a constant at infinity is

$$\begin{aligned} N(\mathbf{r}) &= A \sinh(\kappa r)/(\kappa r) \quad \text{for } 0 \leq r \leq R \ , \\ N(\mathbf{r}) &= N_0(1 - (l/r)) \quad \text{for } r > R \ , \end{aligned} \tag{3.9}$$

with l given by

$$l = R\left[1 - \frac{\tanh(\kappa R)}{(\kappa R)}\right] \equiv R F(\kappa R) \ . \tag{3.10}$$

Accordingly, from Eq. (3.6), we find that the ratio of the total absorption rate of the spherical region to the absorption rate that would be obtained for a single spherical sink of radius R is simply

$$J_T/(4\pi D_0 N_0 R) = F(\kappa R) \ . \tag{3.11}$$

In Fig. 2 $J_T/(4\pi D_0 R N_0)$ is plotted versus (κR). We note that

$$F(\kappa R) \to 1 - (\kappa R)^{-1} + \cdots \quad \text{as } \kappa R \to \infty \ ; \tag{3.12}$$

in this limit J_T approaches the classical rate for a single absorbing sink of radius R. In the opposite limit,

$$F(\kappa R) \to \tfrac{1}{3}(\kappa R)^2 - \tfrac{2}{15}(\kappa R)^4 + \cdots \quad \text{as } (\kappa R) \to 0 \ , \tag{3.13}$$

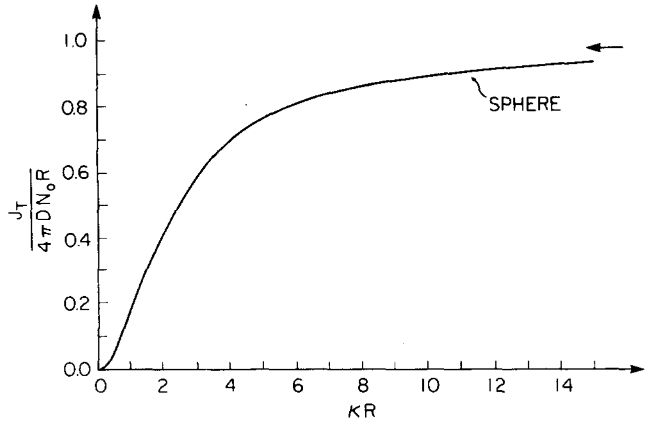

FIG. 2. The ratio of the total absorption rate J_T of a spherical region of radius R containing a uniform density of absorbing sinks to the classical Smoluchowski rate as a function of κR where κ^{-1} is the penetration length of the diffusing molecules into the region.

so that

$$J_T \to (4\pi D_0 a N_0)\mathfrak{N}\,, \tag{3.14}$$

which indicates that the sinks are sufficiently dilute that the total absorption rate is simply $\mathfrak{N}$, the number of sinks, times the absorption rate for each individual sink. It is clear that the physical interpretation of κ^{-1} is that of a penetration length. For $(\kappa R) \ll 1$, the diffusing molecules penetrate into the spherical region without appreciable interference and one recovers the result of absorption into independent sinks. For $(\kappa R) \gg 1$ the diffusing molecules are absorbed directly on entry into the absorbing region and one recovers the result for an absorbing spherical region of radius R.

It is also of interest to inquire how much the absorption rate J_T is reduced by the random removal of absorbing sinks from the region V. Consider the spherical region V of radius R to be constructed from absorbing sinks of radius a in closest packing. The resulting assembly has an effective radius $R' = (R + a)$. Since the volume excluded by each spherical sink is $(4\sqrt{2}a^3)$, the maximum number density of sinks is $\rho_M = [4\sqrt{2}a^3]^{-1}$. If a fraction of the sinks ξ is randomly removed the resulting density will be $\rho = \rho_M(1-\xi)$. According to Eq. (3.8) we have

$$\kappa R' = [(\pi/\sqrt{2})(1-\xi)]^{1/2}(R'/a)\,, \tag{3.15}$$

so that the total absorption rate when ξ spheres are randomly removed $J_T(\xi)$ is

$$J_T(\xi)/[4\pi D_0 N_0 R'] = F(\kappa R')\,. \tag{3.16}$$

For cases where $(R/a) \gg 1$ for a wide range of ξ i.e., $0 < \xi < [1 - (a/R)]$ an adequate approximation is

$$\frac{J_T(\xi)}{4\pi D_0 R N_0} = 1 + \left(\frac{a}{R}\right)\left[1 - \frac{1}{\sqrt{\frac{\pi}{\sqrt{2}}(1-\xi)}}\right]. \tag{3.17}$$

In Fig. 3 the ratio $[J_T(\xi)/J_T(0)]$ is plotted versus ξ for $(R'/a) = 10$, according to Eq. (3.16). The remarkable feature of this result is the slow falloff in absorption rate with the fraction of spheres removed. For example one finds that the total absorption rate is only reduced by 10% when 90% of the spherical sinks are removed. This result reflects the huge excess of sinks that are present when $\kappa R' \gg 1$. In this case the molecule density is low and the reacting molecules are absorbed close to the surface of the spherical region. However, even for a spherical shell the reduction in absorption is small when a fraction of the spheres is removed, as has been shown for a very similar effect which arises in frictional properties of dilute polymer solutions.[4,5] Here, the hydrodynamic interaction strongly modifies the free draining flow of solvent through polymer segments and, as a result, the transport coefficients are quite insensitive to the fraction of segments removed from the polymer structure.

The results of this section can easily be extended to the case where the coefficients for absorption and diffusion have values k and D in the region with uniform distribution of sinks and values k_0 and D_0 outside this region. In the following section we give explicit results in this case for the total reaction rate of the uniform sphere [Eq. (III.6)].

IV. SHAPE FACTORS FOR CATALYTIC PARTICLES

It is evident that solutions of the steady-state continuum equation, Eq. (3.1), will depend upon the *shape* of the region V that contains the density of absorbing sinks $\rho(r)$. Accordingly regions of different shape V will exhibit different total absorption rates J_T. In chemical engineering science one encounters this problem in the determination of "shape factors" for porous catalytic pellets of irregular geometry[6] when diffusion to the catalytic pellet is the rate determining step.

For a single catalytic pellet the shape factor η is defined as the ratio of the total material reacted in the catalytic pellet J_T to the material that would be reacting at perfectly absorbing spherical pellet of the same vol-

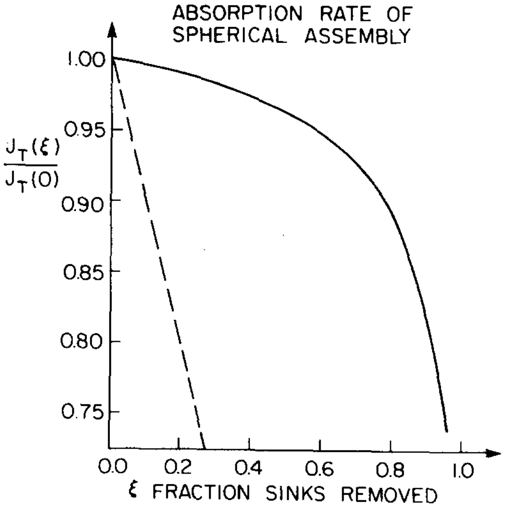

FIG. 3. The ratio of the absorption rate of the spherical assembly $J_T(\xi)$, where a fraction ξ of the sinks has been randomly removed to the rate when $\xi = 0$. The dotted line is the predicted dependence if there were no interaction among the sinks.

ume. Thus for a pellet of volume V and arbitrary shape

$$\eta = J_T/(4\pi D R N_0) \ , \tag{4.1}$$

where R is determined by $(4\pi/3)R^3 = V$. Clearly the shape factor η will depend upon both the pellet geometry and the porosity. For example, the analysis presented in the previous section leads to a value of η for a uniform spherical distribution of sinks according to Eq. (3.11),

$$\eta = F(\kappa R) \ , \tag{4.2}$$

where $\kappa R = \sqrt{4\pi a\rho}R$ and

$$F(x) = 1 - \frac{\tanh(x)}{x} \ . \tag{4.3}$$

Some years ago Aris[7] presented the following expression for the shape factor for a porous sphere

$$\eta_A = [(\kappa R)\coth(\kappa R) - 1] \equiv E(\kappa R) \ . \tag{4.4}$$

Aris arrives at this result by solving Eq. (3.7) with the boundary condition that the ambient concentration N_0 was maintained at the surface of the spherical pellet. As a result

$$N(\mathbf{r}) = N_0 \frac{\sinh(\kappa r)}{\sinh(\kappa R)}\left(\frac{R}{r}\right) \tag{4.5}$$

and the shape factor Eq. (4.4) is obtained. In fact the two shape factors do differ dramatically. The function $E(x)$ behaves as

$$E(x) \to \frac{x^2}{3} - \frac{x^4}{45} + O(x^6) \quad \text{as } x \to 0 \ ,$$

which is similar to $F(x)$ [see Eq. (3.13)]. However as $\kappa R = x$ becomes large $E(x) \to x$, while $D(x) \to 1$ [see Eq. (3.12)]. Of course the difference between these two results has its origin in the difference in the treatment of diffusion external to the pellet.

We have so far considered the case where the diffusion coefficient inside the particle D is identical to the diffusion coefficient outside the particle D_e. Aris assumes that the ambient concentration is maintained at the pellet surface amounts to the statement $(D_e/D) \to \infty$, i.e., diffusion is not a limitation in mass transport to the pellet. Such an assumption seems plausible at first sight in the context of the primary engineering application of packed catalytic beds where the reacting fluid is passed through the bed at an imposed flow rate. However, for a single pellet fixed in the flow of the reacting fluid, it is not true that a uniform concentration is established at the pellet surface.[8] For a bed of pellets the mechanism by which a uniform surface concentration would be established is by no means clear.

Of course it is possible to determine the shape factor for a spherical pellet for arbitrary ratio (D/D_e) of the diffusion coefficient outside the pellet D_e. The result is

$$\eta = \frac{(D_e/D)[1 - \tanh(\kappa R)/(\kappa R)]}{\{1 - [1 - (D_e/D)]\tanh(\kappa R)/(\kappa R)\}} \ , \tag{4.6}$$

where now $\kappa^2 = \kappa\rho/D = 4\pi a_{\text{eff}}\rho$ with effective sink radius a_{eff}. For $(D_e/D) \to 1$ we recover our result Eq. (4.2) while for $(D_e/D) \to \infty$ we recover the result of Aris Eq. (4.4). It should also be kept in mind that the general theory we have developed[1] [see Eq. (2.9)] suggest that $(D_e/D) < 1$, which will lead to a more extreme departure from the Aris result than from Eq. (4.2).

V. COAGULATION AND BURNING

In two applications of classical diffusion controlled reaction theory there is a direct relationship between the absorption rate and the change in volume and mass of the sink. The first application concerns coagulation where the flux of particles absorbed causes the growth of the colloid particle. The second application arises in the simplest theory[9] of combustion where one imagines that the rate at which a liquid drop is burned away is determined by the diffusion rate of oxidant to the flame surface.

When a single spherical sink is present the rate of growth or decay of the spherical region is given by

$$\rho_r(dV/dt) = \pm 4\pi D_0 N_0 m a(t) \ , \tag{5.1}$$

where ρ_r is the mass density (assumed constant) of the sink material, N_0 is the ambient number density of the particles absorbed, m is the mass acquired or lost in a single reaction event, V is the volume of the sink:

$$V(t) = \tfrac{4}{3}\pi a^3(t) \tag{5.2}$$

and the positive and negative sign refer, respectively, to growth or shrinking of the sink volume. The differential equation (5.1) may be re-expressed in terms of the radius squared $a^2(t)$ as

$$\frac{da^2(t)}{dt} = \pm 2\left(\frac{D_0 N_0 m}{\rho_r}\right) \equiv \pm\frac{\lambda}{4} \ , \tag{5.3}$$

which may easily be integrated to yield the well known "d^2 linear law" for the diameter $d = 2a$

$$d^2(t) - d^2(0) = \pm\lambda t \ , \tag{5.4}$$

where λ is the constant defined by Eq. (5.3). The d^2 law holds surprisingly well for both coagulation and combustion.[10]

Of course the association of the steady-state diffusion rate with the particle growth rate is necessarily approximate. Any change in the radius of the absorbing sink will require an adjustment in the density profile outside the sink. The approximate picture adopted here is that the time required to reach the steady state appropriate to a new particle size is very short compared to the characteristic time for the sink to change its size by an appreciable amount. Such a separation of times can be achieved provided $(N_0 m/\rho_r)$ is sufficiently small.

If more than a single sink is present one can expect deviations from the simple linear law Eq. (5.4) due to the competition between the sinks. The growth rate for the volume $V_l(t)$ of sink l, according to the microscopic model, is

$$\rho_r(dV_l/dt) = \pm 4\pi D_0 m q_l = \pm m j_l \ , \tag{5.5}$$

where use has been made of Eq. (2.2) and the + and − sign refer, respectively, to the case of growth or shrinkage of the sink. For $\mathfrak{N}$ spherical sinks one finds from Eqs. (5.5) and (2.3) the coupled microscopic equations

$$\rho_r \frac{dV_i}{dt} = \pm 4\pi D_0 N_0 m a_i(t) - \sum_{j(\neq i)}^{\mathfrak{N}} \frac{a_i(t)\rho_r}{r_{ji}} \frac{dV_j}{dt} . \qquad (5.6)$$

In the case of two sinks one obtains the following modified rate equation for the sink radii:

$$\frac{da_1^2}{dt} = \pm \frac{\lambda}{4} - \frac{a_2}{r_{12}} \frac{da_2^2(t)}{dt} , \qquad (5.7)$$

where a_1 (a_2) refers to the radius of sink 1 (2). An identical equation holds when the subscripts 1 and 2 are interchanged in Eq. (5.7). Hence one deduces:

$$\frac{d}{dt}\left[d_1^2(t) + \frac{1}{3r_{12}} d_2^3(t)\right] = \pm \lambda , \qquad (5.8)$$

which clearly exhibits the modification to the linear d^2 law. Thus due to competition, the sinks grow or shrink less rapidly than they would individually.

The influence of the changing size of the absorbing sinks on the continuum description presented in Sec. III will be substantial. The major effort is to introduce an explicit time dependence into the local shielding length which is defined, in analogy to Eq. (3.8), as

$$\kappa^2(\mathbf{r}, t) = k_0(\mathbf{r}, t)\rho(\mathbf{r})/D_0 = 4\pi\rho(\mathbf{r})a(\mathbf{r}, t) ,$$

where $\rho(\mathbf{r})$ denotes the number density of sinks and $a(\mathbf{r}, t)$ denotes the spherical radius of the sink located at position $\mathbf{r}$ at time t. Qualitatively this time dependence of the shielding length arises because the absorptive capacity of a small region of the medium depends upon the size of the sinks which in turn depends upon the prior history of diffusion and growth in size of the sink. Clearly it is not necessary that the initial distribution of sink sizes in the medium remains undistorted over time. We do not pursue this point further here except to note the connection to kinetics of precipitation from supersaturated solutions.[11]

VI. CONCLUDING REMARKS

A vast variety of phenomena of physical and chemical interest rely on the theory of diffusion controlled reactions. These phenomena include colloid coagulation, precipitation, intrachain reactions of polymers, burning, mass transfer in catalysis, as well as the more familiar application to chemical kinetics. Most of the treatments that employ diffusion theory neglect the interaction between absorbing (or emitting) sinks and investigate only the limit of infinite dilution. In a previous article a general theory was developed to handle the higher concentration effects. In this article some of the implications of the competition between many sinks was explored. Future work will be concerned with kinetics of precipitation, burning, or chemical reaction where these concentration effects cannot be ignored. Special attention[12] will be devoted to the difference between single droplet and spray burning. The burning rate of a spray is not simply the sum of the burning rates of the individual drops in the spray. Significant effects arise from the competition for oxidant, which under restricted circumstances, is governed by a diffusion process. The effect of heat flow in the spray can be considered in a similar manner.[12]

*Supported by the NATO Research Grants Program and, in part, by the National Science Foundation.

[1] B. U. Felderhof and J. M. Deutch, J. Chem. Phys. **64**, xxxx (1976), hereafter referred to as I.

[2] For a similar calculation see E. Paul and R. M. Mazo, J. Chem. Phys. **51**, 1102 (1969).

[3] B. U. Felderhof and J. M. Deutch, J. Chem. Phys. **62**, 2391 (1975). J. M. Deutch and B. U. Felderhof, J. Chem. Phys. **62**, 2398 (1975).

[4] V. Bloomfield, W. O. Dalton, and K. E. van Holde, Biopolymers, **5**, 135, 149 (1967).

[5] J. A. McCammon, J. M. Deutch and B. U. Felderhof, Biopolymers, **14**, 2613 (1975).

[6] C. N. Satterfield, *Mass Transfer in Hetrogeneous Catalysis* (MIT, Cambridge, 1970), Chap. 3.

[7] R. Aris, Chem. Eng. Sci. **6**, 262 (1957).

[8] B. Levich, *Physiochemical Hydrodynamics* (Prentice-Hall, Englewood Cliffs, NJ, 1962) p. 80 ff.

[9] See for example, F. A. Williams, *Combustion Theory* (Addison-Wesley, Reading, 1965), p. 47.

[10] A. Williams, Comb. Flame **21**, 1 (1973); J. F. Rex, A. E. Fuhs, and S. S. Penner, Jet Propul. **26**, 179 (1956).

[11] I. M. Lifshitz and V. V. Slezov, Soviet Phys. JETP **35**, 331 (1959) [Translated from J. Exp. Theor. Phys. (USSR) **35**, 479 (1958)].

[12] Michael J. Saxton, Ph.D. thesis (Harvard University, 1976).