Influence of the spatial distribution of reactive centers on diffusion controlled reactions

S. F. Burlatsky
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 and Institute of Chemical Physics, USSR Academy of Sciences, Kosygin St. 4, 117224, Moscow V-334, Russia

O. F. Ivanov
Institute of Chemical Physics, USSR Academy of Sciences, Kosygin St. 4, 117224, Moscow V-334, Russia

J. M. Deutch
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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The influence of the spatial distribution of fixed reactive centers on the diffusion controlled kinetics of reagent particles is investigated on the basis of a mean-field method for the reaction rate. The reaction kinetics are analyzed in systems where the reactive centers are randomly distributed on the sphere, a line, an array of lines, and other geometrical structures imbedded in two and three dimensions. Finite-size effects influence the time dependence of the reaction rate on different time scales as a result of the competition for the diffusing particles by the fixed reactive centers.

I. INTRODUCTION

In this paper we analyze the kinetics of the reversible reaction

$$A + B \underset{k_-}{\overset{k}{\rightleftarrows}} B \tag{1}$$

in space dimensions $d = 2,3$ when the reactive centers B are localized in particular geometric structures—a line or array of lines, a shell (ring), or a sphere (circle). We demonstrate how the time-dependent kinetics are determined by the competition between the different elements B for the flux of the diffusing substrate A.

Our motivation in addressing this problem is to describe the time dependence of the rate coefficient that will be observed in systems where reaction takes place at inhomogenities that may be present in materials either by design or naturally.

The diffusion of the A particles is described by

$$\frac{\partial \rho}{\partial t}(\mathbf{r},t) = D\nabla^2 \rho(\mathbf{r},t), \tag{2}$$

where $\rho(\mathbf{r},t)$ is the local concentration and D the diffusion coefficient. At the boundaries of the N fixed spherical reaction centers B located at position $\{\mathbf{R}_i\}$, one has the boundary conditions:

$$\left(S^{(d)} D \frac{\partial \rho}{\partial r} + k\rho - k_- \right)_{|\mathbf{r}-\mathbf{R}_i| = a} = 0, \quad i = 1,\dots,N. \tag{3}$$

Here $a = R_A + R_B$ where R_A and R_B are the radii of the particles A and B,

$$S^{(d)} = 2\pi^{d/2} a^{d-1} \Gamma^{-1}(d/2)$$

is the surface area of a d-dimensional spherical region, and $\Gamma(x)$ is the gamma function.

The macroscopic rate equation for reaction scheme (1) is of the form

$$\frac{\partial \rho}{\partial t} = -k^{\text{obs}}(t)\rho(t)n + k_-^{\text{obs}}(t)n, \tag{4}$$

with

$$k^{\text{obs}}(t)/k_-^{\text{obs}}(t) = k/k_- \tag{5}$$

and n is the average density of fixed B centers. We seek explicit expressions for $k^{\text{obs}}(t)$ for various geometries of interest.

II. MODEL DESCRIPTION

Several researchers have addressed this problem.[1-15] Our work extends previous efforts by (i) examining the time dependence of the macroscopic rate coefficient explicitly, (ii) including the influence of reverse reaction, and (iii) analyzing a wider range of topological shapes. Our approach is similar to the approach adopted by previous workers.[2,7,11,13-15]

After Laplace transformation

$$\hat{\rho}(\mathbf{r},z) = \int_0^\infty \rho(\mathbf{r},t) e^{-zt} dt, \tag{6}$$

Eqs. (4) and (5) take the form

$$D\nabla^2 \hat{\rho}(r,z) = z\hat{\rho}(r,z) - \rho_0, \tag{7}$$

where ρ_0 is the initial concentration which we assume to be uniform, and

$$\left(S^{(d)} D \frac{\partial \hat{\rho}}{\partial \mathbf{r}}(\mathbf{r},z) + k\hat{\rho}(\mathbf{r},z) - (k_-/z) \right)_{|\mathbf{r}-\mathbf{R}_i| = a} = 0, \quad i = 1,\dots,N. \tag{8}$$

We seek a solution to Eq. (7) in the form

$$\hat{\rho}(\mathbf{r},z) = \frac{\rho_0}{z} + \sum_{i=1}^{N} c_i G(\mathbf{r}-\mathbf{R}_i;z), \tag{9}$$

where $G(\mathbf{r}_i,z) \equiv G(\mathbf{r})$ is the Green's function solution to the equation

$$q^2 G(\mathbf{r}) - \nabla^2 G(\mathbf{r}) = (S^{(d)}/a^{d-1})\delta(\mathbf{r}), \quad q^2 = (z/D). \tag{10}$$

The explicit expressions for $G(r)$ are

$$G(r) = r^{-1}\exp(-qr), \quad d=3$$

$$G(r) = K_0(qr), \quad d=2 \tag{11}$$

where $K_0(qr)$ is the modified Bessel function of zeroth order. For small x

$$K_0(x) = -\ln x + \text{const.} \tag{12}$$

The coefficients c_i are determined from the boundary conditions Eq. (8). We determine the boundary condition approximately and accordingly incur an error in the treatment. We assert the boundary condition as an average over the surface of the reaction centers. This is valid to order (a/R_{ij}). The flux terms for $j \neq i$ vanish, as can be verified by application of Gauss' theorem neglecting terms of order q^2G.

The result one obtains is the system of linear equations

$$G_0(z)c_i + \sum_{(j\neq i)} G_{ij}(z)c_j = b, \quad i-1,\ldots,N, \tag{13}$$

where

$$b = [(k_-/k) - \rho_0]z^{-1}, \tag{14}$$

$$G_0(z) = G(a) + \frac{S^{(d)}D}{ka^{d-1}}, \tag{15}$$

and

$$G_{ij}(z) = G(|\mathbf{R}_i - \mathbf{R}_j|;z) \equiv G(\mathbf{R}_i - \mathbf{R}_j).$$

The total flux $\hat{J}(z)$ is equal to

$$\hat{J}(z) = -S^{(d)}D\sum_{i=1}^{N} c_i \left(\frac{\partial G(r-R_i)}{\partial|r-R_i|}\right)_{|r-R_i|=a}. \tag{16}$$

When this is evaluated approximately by averaging over the sink surface and employing Gauss theorem one finds

$$\hat{J}(z) = -\frac{S^{(d)}D}{a^{d-1}}\sum_i c_i, \tag{17}$$

neglecting additional terms of order q^2.

Of course both the substrate density $\hat{\rho}(z)$ and the total flux $\hat{J}(z)$ depend upon the position of the N reactive centers through the coefficients $\{c_i\}$. In order to obtain the appropriate macroscopic equations one must average these expressions over the spatial positions of the reactive centers.

III. THE AVERAGE EQUATIONS

We express the discrete set of equations (13) in continuous form as

$$G_0(z)c(\mathbf{r})n(\mathbf{r}) + \int d\mathbf{r}' G(\mathbf{r}-\mathbf{r}')P(\mathbf{r},\mathbf{r}')c(\mathbf{r}') = bn(\mathbf{r}), \tag{18}$$

where

$$n(\mathbf{r}) = \sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{r}_i),$$

$$c(\mathbf{r})n(\mathbf{r}) = \sum_{i=1}^{N} c_i\delta(\mathbf{r}-\mathbf{r}_i), \tag{19}$$

and

$$P(\mathbf{r},\mathbf{r}') = \sum_{i=1}^{N}\sum_{j(\neq i)}\delta(\mathbf{r}-\mathbf{r}_i)\delta(\mathbf{r}'-\mathbf{r}_j).$$

In this continuous representation

$$\rho(\mathbf{r},z) = \frac{\rho_0}{z} + \int d\mathbf{r}' G(\mathbf{r}-\mathbf{r}')c(\mathbf{r}')n(\mathbf{r}') \tag{20}$$

and the flux $\hat{J}$ is given by

$$\hat{J}(z) = \frac{-S^{(d)}D}{a^{d-1}}\int d\mathbf{r}\, c(\mathbf{r})n(\mathbf{r}). \tag{21}$$

The quantities $c(\mathbf{r})$, $n(\mathbf{r})$, and $P(\mathbf{r},\mathbf{r}')$ depend implicitly on the positions of the reactive centers. We next average over the positions of the reactive centers in the geometric region Ω which they occupy. This average will involve products of the dynamical quantities but we shall make a *mean-field approximation* and break these averages of products into products of averages. The result is

$$G_0(z)\bar{c}(\mathbf{r}) + \int d\mathbf{r}' G(\mathbf{r}-\mathbf{r}')\bar{P}(\mathbf{r}'|\mathbf{r})\bar{c}(\mathbf{r}') = b, \tag{22}$$

where

$$\bar{P}(\mathbf{r}'|\mathbf{r}) = \bar{P}(\mathbf{r}',\mathbf{r})/\bar{n}(\mathbf{r}'). \tag{23}$$

In general, $\bar{P}(\mathbf{r}'|\mathbf{r})$ will reflect correlations in the location of particles at position $\mathbf{r}'$ given a particle is present at position $\mathbf{r}$. We shall restrict attention to *uniform distribution* of the reactive centers in the region Ω so that Eq. (22) becomes

$$G_0(z)\bar{c}(\mathbf{r}) + n\int_\Omega d\mathbf{r}' G(\mathbf{r}-\mathbf{r}')\bar{c}(\mathbf{r}') = b \tag{24}$$

and the flux

$$\hat{J}_{\text{av}}(z) = \frac{-S^{(d)}D}{a^{d-1}}\, n\int_\Omega d\mathbf{r}'\bar{c}(\mathbf{r}). \tag{25}$$

In general, it is not possible to determine $\bar{c}(\mathbf{r})$ explicitly from the integral equation (24). However, a rough approximation that will incur some error is given by

$$\int_\Omega \bar{c}(\mathbf{r})dr = \frac{b\Omega}{\left[G_0(z) + n\int_\Omega d\mathbf{r}G(\mathbf{r})\right]} \tag{26}$$

and, hence, for the flux

$$\hat{J}_{\text{av}}(z) = \frac{-S^{(d)}D}{a^{d-1}}N(-b)\quad\left(G_0(z) + n\int d\mathbf{r}\, G(\mathbf{r})\right). \tag{27}$$

If the value of the integral in the denominator of Eq. (27) does not depend on the origin (as is the case for the spherical shell or ring), Eqs. (26) and (27) provide an exact solution of Eq. (24). We evaluate Eq. (26) by placing the origin at the center of mass of Ω and, hence, incur an underestimate of the flux.

From Eqs. (14) and (27) we find that the Laplace transform of the steady-state average flux is proportional to the factor $[\rho_0 - (k_-/k)]N$ under circumstances when the density of reacting species is kept constant at large distances from the reactive sinks. Strictly speaking we cannot make an identification with the time-dependent rate coefficient as exhibited in Eq. (4). The difficulties that are encountered in making this identification have been discussed by Bixon and Zwanzig.[16] Nevertheless, we believe that a reasonable argument can be made from noting that the average flux can be put in the form

$$J_{\rm av}(t) = -\hat{k}^{\rm obs}(t)\left(\rho_0 - \frac{k_-}{k}\right)N.$$

The macroscopic rate equation Eq. (4) at a large distance from the region Ω which contains the reactive sinks will have the form

$$\Omega\frac{\partial\rho}{\partial t} = -k^{\rm obs}(t)\left(\rho(t) - \frac{k_-}{k}\right)N,$$

where use has been made of Eq. (5)

We assert that the time-dependent rate coefficients for the case of uniform substrate density will be the same as for the case of time-dependent substrate density. Thus, we make the identification $\hat{k}^{\rm obs}(t) = k^{\rm obs}(t)$ while acknowledging the possibility that differences may exist between these two coefficients as suggested by the analysis in Ref. 16.

IV. RESULTS FOR THREE DIMENSIONS

For three-dimensional systems, according to Eqs. (15) and (11),

$$\hat{J}_{\rm av}(z) = \frac{4\pi DN(-b)}{[(e^{-qa}/a) + (4\pi D/k) + nI(q)]}, \tag{28}$$

where

$$I(q) = \int_\Omega dr(e^{-qr}/r). \tag{29}$$

We will consistently assume $t \gg t_a = a^2/D$, so that $(qa) \ll 1$. This leads to

$$\hat{J}_{\rm av}(z) = \frac{k_{\rm SCK}N[\rho_0 - (k_-/k)]}{z + nk_{\rm SCK}(q^2/4\pi)I(q)}, \tag{30}$$

where $k_{\rm SCK}$ is the Smoluchowski–Collins–Kimball rate coefficient,[1]

$$k_{\rm SCK} = \frac{4\pi Dak}{k + 4\pi Da}. \tag{31}$$

We proceed to evaluate $\hat{J}_{\rm av}(z)$ for several three-dimensional geometries of interest.

A. The sphere

For this geometry

$$I(q) = (4\pi/q^2)[1 - (1 + qR)e^{-qR}]. \tag{32}$$

In the limit $(qR) \gg 1$, i.e., $t \ll \tau_R = R^2/D$, the integral $I(q) \to (4\pi/q^2)$ and, hence,

$$\hat{J}_{\rm av}(z) = \frac{k_{\rm SCK}N[\rho_0 - (k_-/k)]}{z + nk_{\rm SCK}}, \quad N = 4\pi R^3 n/3. \tag{33}$$

The resulting rate coefficient is

$$k^{\rm obs}(t) = k_{\rm SCK}\exp[-k_{\rm SCK}nt]. \tag{34}$$

This corresponds to each reactive center acting independently.

For $(qR) \ll 1$, i.e., $t \gg \tau_R$, the integral $I(q) \to 2\pi R^2$,

$$\hat{J}_{\rm av}(z) = \frac{k_{\rm SCK}k_n}{k_{\rm SCK} + k_n}N\frac{1}{z}[\rho_0 - (k_-/k)], \tag{35}$$

where $k_n = (2D/nR^2)$. In this limit k_n should equal $(3D/nR^2)$ so the factor (2/3) provides an indication of the magnitude of the error incurred in the approximation leading to Eq. (26). For this case, the reactive centers effectively act as a single reactive sphere of radius R and one finds

$$k^{\rm obs} = \frac{k_{\rm SCK}k_n}{k_{\rm SCK} + k_n}. \tag{36}$$

It is possible to solve the mean-field equation exactly for the case of the sphere and a few other geometries of interest. In the Appendix we compare the exact mean-field solution for the sphere with the results obtained here in order to give a better basis for assessing the consequence of the approximation made in passing to Eq. (27).

B. Particles on a line

If the reactive sinks are uniformly distributed on a line of length L (and radius a), the screening integral $I(q)$ is

$$I(q) = 2\int_{(-L/2)}^{(L/2)}\frac{e^{-qr}}{r}dr = 2[E_1(qa) - E_1(qL)]$$
$$= \begin{cases} -2\ln(qa) & \text{if } qa \ll 1,\ qI \gg 1 \\ 2\ln(L/a) & \text{if } (qL) \ll 1. \end{cases} \tag{37}$$

Here $E_1(x)$ is the exponential integral function.

For times $t \ll (L^2/D) \equiv \tau_L$, the finite length of the line of traps is not apparent and Eq. (28) for the flux becomes

$$\hat{J}_{\rm av}(z) = \frac{k_{\rm SCK}N[\rho_0 - (k_-/k)]}{z[1 - 2n(k_{\rm SCK}/4\pi D)\ln(qa)]}, \quad N = nL. \tag{38}$$

For short times $(k_{\rm SCK}/2\pi D)n\ln(qa)^2 \ll 1$, i.e., $t < \tau_{al}\exp[2\pi D/nk_{\rm SCK}] \equiv \tau_1$, the flux describes reaction to N-independent sinks. For times $t > \tau_1$ (if $\tau_1 < \tau_L$) there is competition between the sinks. The forward time-dependent rate coefficient is approximately

$$k^{\rm obs}(t) = \frac{4\pi D}{n\ln(Dt/a^2)}, \tag{39}$$

which is similar to the Smoluchowski solution for diffusion of particles to a perfect cylindrical trap.

For times $t \gg \tau_L$, the kinetics reflects the finite size of the line and will again exhibit steady-state behavior. In this limit the rate coefficient becomes

$$k^{\rm obs} \approx \frac{2\pi D}{n\ln(L/a)}. \tag{40}$$

C. An array of lines

We next imagine that the N traps are distributed uniformly on lines of length L and that lines of these traps are uniformly distributed parallel to an axis. This system will exhibit the following sequence of behavior: independent reactive centers, a single line, an array of lines, and finally the cluster of lines.

We assume that each line of length L contains n reactive center per unit length and that there are σ such lines per unit area arranged in a finite cluster of area $A = \pi L^2$. Thus, the total number of reactive sinks is $N = \sigma \pi L^2 nL$.

The shielding integral $I(q)$ equals the sum of the single line contribution in Eq. (37) and a term $I_2(q)$ arising from the neighboring lines,

$$I_2(q) = 2\pi s \int_a^L dr\, r^2 \int_0^L \frac{\exp[-q(x^2+r^2)^{1/2}]}{(x^2+r^2)^{1/2}}\, dx. \tag{41}$$

This integral has the following limits:

$$\begin{aligned} &I_2 \to 4\pi\sigma/q^2, \quad qa \ll 1,\ qL \gg 1,\\ &I_2 \to 8\pi\sigma L^2, \quad qL \ll 1. \end{aligned} \tag{42}$$

For times $t \ll \tau_L$, the flux has the form

$$\hat{J}_{\rm av}(z) = \frac{k_{\rm SCK} N[\rho_0 - (k_-/k)]}{k_{\rm SCK}\sigma n + z[1 - 2k_{\rm SCK}(n/4\pi D)\ln(qa)]}. \tag{43}$$

For short times $t < \tau_1$, leads to a forward rate reflecting independent sinks

$$k^{\rm obs}(t) = k_{\rm SCK} \exp(-k_{\rm SCK}\sigma n t). \tag{44}$$

This expression is of the same form as Eq. (34) but with a different effective concentration.

For times $\tau_1 < t < \tau_L$, the flux takes the form

$$\hat{J}_{\rm av}(z) = \frac{4\pi DN}{n \ln[1/(qa)^2]} \frac{[\rho_0 - (k_-/k)]}{z + \{(\sigma 4\pi D)\ln[1/(qa)^2]\}}, \tag{45}$$

which leads to a forward rate coefficient of the form

$$k^{\rm obs}(t) = \frac{4\pi D}{n \ln[Dt/a^2]} \exp\left(-\frac{4\pi\sigma Dt}{\ln(Dt/a^2)}\right). \tag{46}$$

For long time $t > \tau_L$, a steady state is approached. It is easy to determine this rate to be

$$k^{\rm obs} = \frac{k_{\rm SCK} k_n}{k_{\rm SCK} + k_n},$$

where

$$k_n = \frac{2\pi D}{n[4\pi\sigma L^2 + \ln(L/a)]}. \tag{47}$$

For low density of lines, $k^{\rm obs} = k_{\rm SCK}$. For high n and low density of lines $[\ln(L/a) \gg 4\pi\sigma L^2]$ the observed rate $(k^{\rm obs}N)$ will approach the value for $(\pi L^2\sigma)$ independent lines each contributing $[2\pi DL/\ln(L/a)]$ to the rate coefficient. For a high density of lines, $(k^{\rm obs}N)$ approaches the value expected for diffusion to a single massive array that appears as an ideal spherical trap of size $R = L/8$. The numerical value (1/8) is approximate.

D. Other three dimensional geometries

Other geometries may be analyzed in a similar fashion. In all cases, the following behavior is found. For short time, $t < \tau_1$, the rate is described by independent sinks; for intermediate times $\tau_1 < t < \tau_L$ the rate coefficient is time dependent reflecting competition among the sinks; for long times $t > \tau_L$ a steady state is approached. For this steady state, at high trap density, the total rate coefficient $(Nk^{\rm obs})$ will have the form of the rate for a single ideal spherical trap with an effective radius $R_{\rm eff}$. The numerical value determined for $R_{\rm eff}$ is only approximate. Table I presents results for three other geometries of traps: a plane, a spherical shell, and a ring.

V. RESULTS FOR TWO DIMENSIONS

The story for reactive centers in two dimensions is very similar to $d = 3$ except that no steady state is attained. We offer an explicit analysis for the case of a circle and simply present results for several other cases.

According to Eq. (27) one finds, for the flux in $d = 2$,

$$\hat{J}_{\rm av}(z) = \frac{2\pi DkN(\rho_0 - k_-/k)(1/z)}{2\pi D - k\ln(aq) + nM(q)k}, \tag{48}$$

where $(aq) \ll 1$ and $M(q)$ is the screening integral

$$M(q) = \int dr K_0(qr). \tag{49}$$

For the circle, the screening integral is

TABLE I. Results for the screening integral and the rate coefficient in different time regimes in three dimensions for various geometries of reactive centers.

Screening integral $I(q)$	$k^{\rm obs}(t)$ $\tau_1 < t < \tau_L$	$k^{\rm obs}$ Steady state	$k^{\rm obs}N/4\pi D = R_{\rm eff}$ $n \to \infty$
		Plane	
$2\pi \int_0^L dr \exp(-qr)$	$\frac{2}{n}\sqrt{D/(\pi t)}$	$k_{\rm SCK}/1 + (nk_{\rm SCK}L/2D)$	$L/2\pi$
		Spherical shell	
$2\pi R^2 \int_0^\pi d\vartheta \frac{\exp[-2qR\sin(\vartheta/2)]}{2R\sin(\vartheta/2)}$	$\frac{2}{n}\sqrt{D/(\pi t)}$	$k_{\rm SCK}/1 + (nk_{\rm SCK}R/D)$	R
		Ring	
$2R\int_{(a/R)}^{2\pi} d\phi \frac{\exp[-2qR\sin(\phi/2)]}{2R\sin(\phi/2)}$	$\frac{4\pi D}{n\ln[Dt/a^2]}$	$k_{\rm SCK}/1 + [nk_{\rm SCK}\ln(2R/a)/\pi D]$	$\pi R/n\ln(2R/a)$

$$M(q) = 2\pi \int_0^r dr\, rK_0(qr)$$
$$= 2\pi/q^2[qaK_0(qa) - qRK_0(qR)].$$

For short times $(qR) \gg 1$, and the screening integral approaches $M(q) \to (2\pi/q^2)$ so that

$$\hat{J}_{\rm av}(z) = \frac{k}{nk + z\{1 - [k\ln(aq)/2\pi D]\}} N(\rho_0 - k_-/k). \tag{50}$$

For times $\tau_a < t < \tau_a \exp(4\pi D/k) \equiv \tau_2$, the observable forward rate is

$$k^{\rm obs}(t) = k\exp(-knt) \tag{51}$$

again reflecting independent action of the sinks.

For times $\tau_2 < t < \tau_L$ we find an approximate expression, for the flux

$$\hat{J}_{\rm av}(z) = \frac{4\pi D}{n4\pi D - z\ln(aq)^2} N(\rho_0 - k_-/k), \tag{52}$$

of the form

$$k^{\rm obs}(t) = k(t)\exp\left[-n\int_0^t d\tau k(\tau)\right], \tag{53}$$

where $k(t)$ has the form of a single $d = 2$ trap,

$$k(t) = \frac{4\pi D}{\ln(Dt/a^2)}. \tag{54}$$

In the long time limit $t > \tau_L$ or $(qR) \ll 1$, the screening integral approaches the value $[-\pi R_2 \ln(qR)]$. Accordingly, the forward rate may be estimated to behave like,

$$k^{\rm obs}(t) = \frac{2\pi Dk}{2\pi D + k(n\pi/2)R^2\ln(Dt/R^2)}. \tag{55}$$

If the density of sinks in the circle is high then the quantity $Nk^{\rm obs}(t)$ approaches

$$k^{\rm obs}(t)N \to 4\pi D/\ln(Dt/R^2), \tag{56}$$

which exactly coincides with the Smoluchowski solution for a single reactive center of radius R in the plane.

A similar analysis can be carried out for other geometries of reactive centers in $d = 2$. Table II presents results for the forward rate $k^{\rm obs}(t)$ for reactive centers arranged in a line, an array of lines, and a ring.

VI. CONCLUDING REMARKS

The point of this work is to demonstrate that the time dependence of the observed rate coefficient of a diffusion controlled reaction is a signature for the geometry of the locations of the fixed reactive centers where reaction takes place. For short times, the reaction time dependence reflects independent centers. At long times, the kinetics eventually follows the time evolution appropriate to a single reactive center with a geometrical factor that depends upon the shape of the localized region that contains the reactive centers. At intermediate times, a particular time dependence arises that reflects the competition between the fixed reactive centers. The inverse problem is also of interest: How to design the geometry of a catalytic region in order to obtain a desired time dependence for the course of a chemical reaction.

TABLE II. Results for the forward observed rate coefficient in two dimensions when reactive centers are arranged in the pattern shown. The results are in the limit $t \gg \tau_L = (L^2/D)$.

Arrangement of reactive centers	$2\pi D/k^{\rm obs}(t)$
Line	$2\pi D + nkL\ln(Dt/L^2)$
Array of lines	$2\pi D + nkL(1 + 4\pi\sigma L)\ln\left(\frac{Dt}{L^2}\right)$
Ring	$2\pi D + nkR\pi\ln(Dt/R^2)$

APPENDIX

In this Appendix we calculate the exact mean-field reactive flux for the sphere in order to provide a basis for assessing the approximation introduced in Eq. (26).

In differential form, the mean-field equation for a sphere of reactive centers is [Eq. (2b), Ref. 14],

$$\frac{\partial\rho(r,t)}{\partial t} = D\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\rho(r,t) - kn\rho(r,t), \quad r<R,$$
$$\frac{\partial\rho(r,t)}{\partial t} = D\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\rho(r,t), \quad r>R, \tag{A1}$$

where we have neglected the reverse reaction and $k = 4\pi Da$ is the rate coefficient for diffusion to the N reactive sites of radius a that are distributed with uniform density $n = N/(4\pi R^3/3)$ in the sphere. These equations must be solved with the boundary conditions that the concentration is finite at the origin of the sphere and approaches ρ_0 at a large distance from the sphere. The concentration and its first derivative are continuous at $r = R$. The initial condition is that the concentration is uniform outside the sphere with a value ρ_0.

In terms of the Laplace transform

$$\bar{\rho}(r,z) = \int_0^\infty dt\exp(-zt)\rho(r,t), \tag{A2}$$

the equations become

$$\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\bar{\rho}(r,z) - \frac{z+kn}{D}\bar{\rho}(r,z) = 0, \quad r<R,$$
$$\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\bar{\rho}(r,z) - \frac{z}{D}\bar{\rho}(r,z) = \frac{-\rho_0}{D}, \quad r>R. \tag{A3}$$

The solution to these equations are

$$\bar{\rho}(r,z) = (\sqrt{R}/\sqrt{r}\Delta)\frac{(\rho_0/qD)I_{1/2}(sr)}{I_{3/2}(sR)}, \quad r<R,$$
$$\bar{\rho}(r,z) = (\sqrt{R}/\sqrt{r}\Delta)\frac{(\rho_0 s/qD)K_{1/2}(qr)}{K_{3/2}(qR)} + \frac{\rho_0}{q^2D}, \quad r>R. \tag{A4}$$

Here $q^2 = (z/D)$, $s^2 = [q^2 + (kn/D)]$, and $I_{n/2}$ and $K_{n/2}$ are modified Bessel functions of fractional order.

The quantity Δ is

$$\Delta = \left(q \frac{I_{1/2}(sR)}{I_{3/2}(sR)} + s \frac{K_{1/2}(qR)}{K_{3/2}(qR)} \right)$$

$$\Delta = \left[q \left(\coth(sR) - \frac{1}{sR} \right)^{-1} + s\left(1 + \frac{1}{qR} \right)^{-1} \right]. \tag{A5}$$

The flux entering the spherical region of reactive sinks is

$$\bar{J}(z) = -4\pi R^2 D \left(\frac{\partial \bar{\rho}}{\partial r} \right)_{r=R} = 4\pi R^2 \rho_0 (s/q) \frac{1}{\Delta} \tag{A6}$$

and the reactive flux is

$$\bar{J}_{rxn}(z) = 4\pi kn \int_0^R dr\, r^2 \bar{\rho}(r,z) - \frac{4\pi kn R^2 \rho_0}{sqD\Delta}. \tag{A7}$$

These are the exact mean-field results for a spherical region of reactive traps. We compare these exact results with the approximate results presented in Sec. IV A.

First, we consider the limit of dense traps $n \to \infty$ which means $s \to \infty$. In this case, all the reaction takes place at the surface of the spherical region. The external flux in this limit approaches

$$\bar{J}(z) = \frac{4\pi R D \rho_0}{z} (1 + qR), \tag{A8}$$

which is the result one expects for reaction with a single sphere of reactive sphere of radius R. As discussed in text, the result from our approximate method Eq. (35) differs by a factor of (2/3).

Next, we consider the reactive flux term Eq. (A7). In the limit $n \to \infty$, $s \to \infty$ we obtain the result Eq. (A8) as expected. In the opposite limit $n \to 0$, the reactive centers are dilute. For long times $q,s \to 0$, one obtains the result

$$\bar{J}_{rxn}(z) = \frac{kN}{z} \frac{1}{1 + [(z + kn)R^2/3D]}. \tag{A9}$$

In this limit, the diffusing particles have penetrated the spherical trap region and the reactive flux arises from N-independent sinks. The leading behavior is identical to Eq. (33) but the corrections differ. This occurs because the approximation Eq. (26) does not accurately describe the diffusion through the reactive sphere.

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