Exact solution for the diffusion controlled rate into a pair of reacting sinks[a)]

René Samson and J. M. Deutch

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

(Received 30 March 1977)

Recently there has been interest in determining the concentration dependence of diffusion controlled reactions.[1–3] The concentration dependence physically arises from the competition for the diffusing species among the reactive sites. This competition has the effect of reducing the effective rate coefficient of an assembly of reactive sites below the value expected from N independent sites, $k_0 = N(4\pi DR)$. Here D is the diffusion coefficient of the reacting species and R is the radius of the reaction center.

In this note, we present an exact solution for the case of two fixed centers $N = 2$ in order to provide a basis for comparison to the more general theories[1] which, however, introduce approximations to deal with the case of greater interest, of large N.

The problem we solve is

$$D\nabla^2 n(\mathbf{r}) = 0, \tag{1}$$

where $n(\mathbf{r})$ is the concentration of the reacting species at point $\mathbf{r}$, subject to the boundary conditions that $n(r) \to n_0$ at large distances from the reaction center pair and that $n(r)$ vanishes at the boundary of the two centers that are separated by a distance l, assigned to lie on the z axis. The solution, which is identical to Laplace's equation for the electrostatic potential surrounding two conducting spheres, is found in terms of bispherical coordinates[4]:

$$n(\mathbf{r})/n_0 = 1 - [2(\cosh\mu - \cos\eta)]^{1/2} \times \sum_{m=0}^{\infty} \frac{\exp[-(m+\frac{1}{2})\mu_0]}{\cosh[(m+\frac{1}{2})\mu_0]} \times \cosh[(m+\tfrac{1}{2})\mu] P_m(\cos\eta), \tag{2}$$

where the coordinates (μ, η, ϕ) are related to the cartesian coordinates (x, y, z) as given in Ref. 4. The rate coefficient is determined by computing the specific flux "disappearing" into both centers. The result is

$$\frac{k(l)}{k_0} = 1 - \sum_{m=2}^{\infty} (-1)^m \frac{\sinh\mu_0}{\sinh m\mu_0}, \tag{3}$$

where the parameter μ_0 is determined by $\cosh\mu_0 = l/2R$. In the limit of infinite separation $l/2R \to \infty$ $(\mu_0 \to \infty)$, the result is $k \to k_0$. At contact $l \to 2R(\mu_0 \to 0)$ the result is $k(2R) = (\ln 2)k_0 = 0.69\ k_0$. The result $k(l)/k_0$ versus separation (l/R) is plotted in Fig. 1.

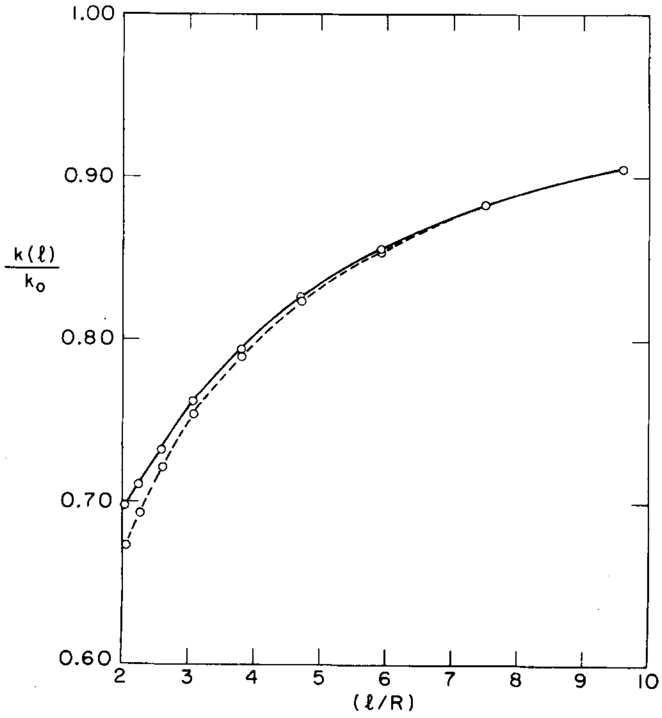

FIG. 1. Reduced diffusion controlled rate coefficient vs separation of reacting sinks. Solid line, exact result, Eq. (3); broken line, approximate result, Eq. (4).

Included in Fig. 1 is the approximate result[5]

$$[k(l)/k_0]_{\text{approx}} = [1 + (R/l)]^{-1} \tag{4}$$

which agrees with Eq. (3) in the large separation limit where $l \to R\exp(\mu_0)$. At contact the approximate expression gives the result $[k(2R)/k_0]_{\text{approx}} = \frac{2}{3}$, which is remarkably close to the exact result when one considers that the approximate method is essentially based on the assumption of large separation. This fortunate agreement suggests that the large separation approximation employed in theories of the concentration dependence of the diffusion controlled rate coefficient may not be too severe.

One of us (J. M. D.) thanks Professor Feshbach for helpful guidance.

[a)] Supported in part by the National Science Foundation.

[1] B. U. Felderhof and J. M. Deutch, J. Chem. Phys. 64, 4551 (1976), and references cited therein.

[2] D. Peak, K. Pearlman, and P. J. Wantuck, J. Chem. Phys. 65, 5538 (1976).

[3] W. Strieder and R. Aris, *Variational Methods Applied to Problems of Diffusion and Reaction* (Springer, Berlin, 1973).

[4] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics*, Part II (McGraw-Hill, New York, 1953), page 1298 ff.

[5] J. M. Deutch, B. U. Felderhof, and M. J. Saxton, J. Chem. Phys. 64, 4559 (1976), and references cited therein.