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Theoretical and Experimental Aspects of Surface Diffusion in Porous Catalysts

I. Nonreactive Conditions

T. T. TSOTSIS, R. C. SANE, I. A. WEBSTER,* AND J. D. GODDARD

*Department of Chemical Engineering, University of Southern California, Los Angeles, California 90089-1211; and *Unocal Science and Technology Division, Unocal Corporation, Brea, California 92621*

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The primary goal of this study is to clarify some very basic questions and outstanding problems in the field of surface diffusion in porous catalysts. Attention is focused on certain mathematical techniques utilized in the past to interpret experimental data. The common assumption of adsorption equilibrium is shown to lead to very serious errors. Two approximate perturbation techniques are presented which lead to analytical expressions for surface diffusion enhancement as a function of the relevant parameters. These expressions are shown to yield good predictions of overall diffusivities. We conclude that similar analyses should be employed to interpret or reevaluate surface-diffusion data and, particularly, to check the adsorption equilibrium assumption. © 1986 Academic Press, Inc.

INTRODUCTION

Surface diffusion in porous catalysts remains one of the least studied and probably least understood phenomena in catalysis. The knowledgeable observer is hard-pressed to understand the lack of scientific interest. Although the existing surface diffusion data is scarce (*1–5*), it clearly points out that surface diffusion is an important mechanism for transporting reactants and products in porous catalysts. In many cases, transport by surface diffusion is at least if not more important than bulk diffusion.

Many works in catalysis discount transport by surface diffusion, on the grounds that the diffusivities are usually two orders of magnitude smaller than the corresponding bulk diffusivities. This is one misconception pointed out in the early seventies by Smith and co-workers (*4, 5*). Although generally true that adsorbed molecules on a catalytic surface move on an average at a slower pace than molecules in the bulk of the adjacent pore space, their numbers can be far greater. As a result, the effect of transport can be as important as bulk diffusion. To visualize this, one needs only to compare the number of riders transported in certain major cities by a (relatively) slow bus system to those conveyed by private automobiles. In another domain, of more relevance, a similar state of affairs may exist for the carrier mediated transport of oxygen in biological systems by (slow but concentrated) carriers such as hemoglobin.

Standard texts in reaction engineering (*6–8*), which typically devote several chapters to different aspects of diffusion in heterogeneous catalysts, give at most sketchy accounts of surface diffusion. Research papers fare only slightly better. Riekert (*9*), in a recent publication, addresses one of the most common misconceptions surrounding the question of adsorption–desorption equilibrium. As he correctly surmises, a strict interpretation of adsorption equilibrium as a condition of zero net rate at all points on the pore surface would effectively rule out transport by surface diffusion. We agree and show below that the question is one of interpretation. On the other hand, Riekert (*9*) draws the rather distressing

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conclusion that it is not possible to determine surface diffusivities experimentally except by measurement of local surface concentration gradients. Although experiments of the above type have been recently reported for single crystal catalysts (*10*), it will probably be years, if ever, before surface gradients can be measured in the typical industrial catalyst pellet. Far from abandoning hope, it is the goal of this paper to show that the effects of surface diffusion can be assessed in an analytical fashion.

In a recent paper, Aris (*11*) has given such an analysis, which in many respects sets the record straight. He correctly points out that effective diffusivities measured in the presence of surface diffusion are strongly dependent on local bulk concentrations. Aris' mathematical treatment is, however, based on a regular perturbation analysis for small concentration gradients, which has a limited region of applicability.

Here we wish to show that more general and powerful techniques are available to treat the problem. In fact, since the mathematical problems are essentially equivalent, practically all the mathematical apparatus required for analysis has already been developed for the facilitated diffusion through membranes (*12–14*). While it is not, therefore, strictly necessary to develop an analysis from the ground up, the present paper, partly didactic in nature, aims to familiarize workers in catalysis with a few basic mathematical aspects of surface diffusion in porous catalysts and, also, to rectify certain frequent misconceptions and incorrect assumptions.

Attention will be focused here on the simplest geometry, a straight cylindrical pore, through which molecular transport occurs by simultaneous bulk and surface diffusion. Such a model, of course, presents an oversimplified description of diffusion in the tortuous porous structure common to most industrial catalysts; but such complexities, the subject of future works (*15*), need not concern us here. At any rate, there exist today several model porous solids (typically polycarbonate or mica sheets and anodized aluminum foils) having physically straight cylindrical pores with very narrow, unimodal pore size distributions and closely mimicing our mathematical idealization. Later in this paper we report some experimentally measured diffusivities for such solids.

THE MATHEMATICAL PROBLEM

We consider a steady state in which the diffusing-species concentration is maintained constant at the ends of a pore (a situation which is conveniently attained experimentally for gaseous systems by means of the typical Kallenbach cell). We deal here with the case of a single diffusing species for which the local bulk and surface diffusional fluxes are given, respectively, as

$$J_{\mathrm{b}} = -D_{\mathrm{b}}\pi r^2 \frac{dC}{dx}, \tag{1}$$

and

$$J_{\mathrm{s}} = -D_{\mathrm{s}}2\pi r \frac{dn}{dx}.$$

The equations describing steady-state diffusion in a single pore then are

$$D_{\mathrm{b}} \frac{d^2C}{dx^2} - g(C, n) = 0, \tag{2}$$

$$D_{\mathrm{s}} \frac{d^2n}{dx^2} + a_{\mathrm{v}}g(C, n) = 0, \tag{3}$$

with

$$C = C_{\mathrm{H}}; \quad \frac{dn}{dx} = 0 \quad \text{at } x = 0 \tag{4}$$

$$C = C_{\mathrm{L}}; \quad \frac{dn}{dx} = 0 \quad \text{at } x = L \tag{5}$$

where $g(C, n)$ denotes the net rate of adsorption on the catalyst surface, that is, the rate of adsorption minus the rate of desorption. As pointed out by Riekert, when adsorption equilibrium is attained, $g(C, n) \equiv 0$ throughout the pore and one concludes from Eqs. (3), (4), and (5) that

$$\frac{dn}{dx} = 0 \quad \text{for} \quad 0 \leq x \leq L, \tag{6}$$

and, hence, that surface diffusional flux is zero. Thus one might erroneously conclude that adsorption equilibrium, assumed in most published studies, implies zero surface transport. This conceptual problem is the result of the peculiar nature of the equilibrium assumption. When invoked on the basis of fast adsorption–desorption kinetics, it represents in mathematical terms a singular perturbation of the type which has been well studied in the context of facilitated transport (*12–14*). As a result, we now appreciate that the no-flux conditions on the surface species in Eqs. (4) and (5) cannot be imposed in this equilibrium limit, owing to the existence of reactive zones at the ends of the pore, $x = 0, L$. This point will be illustrated by the following analysis.

For present purposes, it will be assumed that adsorption and desorption processes are of simple Langmuir type, i.e.,

$$g(C, n) = K_aC(n_t - n) - K_dn. \tag{7}$$

The mathematical analysis described here can be applied to many other complex forms of $g(C, n)$ (*12–14*). To identify the relevant parameters, we take

$$\xi = \frac{x}{L}, \quad X = \frac{C}{C_H},$$

$$\theta = \frac{n}{n_t}, \quad K = \frac{K_aC_H}{K_d} \tag{8}$$

$$\Phi = L\sqrt{\frac{K_an_tC_H}{D_b}}, \quad \zeta = \frac{C_HD_b}{n_ta_vD_s}, \tag{9}$$

and Eqs. (2)–(6) become

$$\frac{d^2X}{d\xi^2} - \Phi^2G(X, \theta) = 0 \tag{8}$$

$$\frac{d^2\theta}{d\xi^2} + \zeta\Phi^2G(X, \theta) = 0 \tag{9}$$

$$X = 1; \quad \frac{d\theta}{d\xi} = 0 \quad \text{at } \xi = 0 \tag{10}$$

$$X = X_L; \quad \frac{d\theta}{d\xi} = 0 \quad \text{at } \xi = 1 \tag{11}$$

with

$$G(X, \theta) = X(1 - \theta) - \frac{\theta}{K}. \tag{12}$$

The phenomenon of surface diffusion is therefore characterized by four dimensionless groups, namely, a Thiele modulus Φ representing the ratio of bulk diffusion to adsorption times; the thermodynamic equilibrium constant K; the ratio of pore-mouth concentrations X_L, and a transport ratio (with $a_v = 2/r$ for a cylindrical pore),

$$\zeta = \frac{D_bC_H}{D_sn_ta_v} \equiv \frac{D_b\pi r^2(C_H - 0)/L}{D_s2\pi r(n_t - 0)/L}, \tag{13}$$

which represents the ratio of characteristic bulk and surface diffusional fluxes. The boundary value problem (8)–(12), can of course be treated numerically, but such an approach does not lend itself easily to experimental parameter identification and sensivity studies. Fortunately there exist a number of asymptotic and approximate analytical methods, which are valid in different regions of the (X_L, Φ, K, ζ) parameter space and which we now apply.

I. Small Gradients and Linearized Kinetic Analysis

Aris (*11*) has given an analysis for $X_L \simeq 1$ or $\varepsilon = 1 - X_L \simeq 0$ (i.e., for $C_H \simeq C_L$) where one can apply the following regular perturbation scheme

$$X(\xi) = X_0(\xi) + \varepsilon X_1(\xi) + \varepsilon^2X_2(\xi) + \ldots \tag{14}$$

$$\theta(\xi) = \theta_0(\xi) + \varepsilon\theta_1(\xi) + \varepsilon^2\theta_2(\xi) + \ldots, \tag{15}$$

where $X_0(\xi) = 1$ and $\theta_0(\xi)$ are solutions of

$$G(X_0, \theta_0) = 0. \tag{16}$$

If one expresses $G(X, \theta)$ in terms of an ε series expansion around X_0, θ_0 then

$$G(X, \theta) = G(X_0, \theta_0) + \left(\frac{\partial G}{\partial \varepsilon}\right)_0 \varepsilon + O(\varepsilon^2)$$
$$= X_1 G_X + \theta_1 G_\theta + O(\varepsilon^2) \qquad (17)$$

with

$$G_X = \left(\frac{\partial G}{\partial X}\right)_0; \quad G_\theta = \left(\frac{\partial G}{\partial \theta}\right)_0, \qquad (18)$$

where subscript zero refers to conditions at $X = X_0$; $\theta = \theta_0$. Substituting Eqs. (14)–(18) into Eqs. (8)–(12), one gets the linear forms

$$\frac{d^2X_1}{d\xi^2} = \Phi^2[G_X X_1 + G_\theta \theta_1] \qquad (19)$$

$$\frac{d^2\theta_1}{d\xi^2} = -\xi\Phi^2[G_X X_1 + G_\theta \theta_1] \qquad (20)$$

$$X_1 = 0; \quad \frac{d\theta_1}{d\xi} = 0 \quad \text{at } \xi = 0 \qquad (21)$$

$$X_1 = 1; \quad \frac{d\theta_1}{d\xi} = 0 \quad \text{at } \xi = 1, \qquad (22)$$

which admit analytical solution. The details can be found in Aris' work (*11*). In experiments on diffusion through porous catalysts, one usually expresses the measured flux in terms of an effective diffusivity and the overall concentration gradient as

$$\text{Flux} = -D_e \left(\frac{C_H - C_L}{L}\right). \qquad (23)$$

Of interest then is the quantity $(D_e/D_b - 1)$, which is the measure of diffusional flux beyond that expected for simple bulk (Fickian or Knudsen) diffusion alone. In the field of facilitated transport through membranes, the above quantity is called the "enhancement" or "facilitation" factor.

Based on the above analysis, we recall that Aris (*11*) has given the following expression for the surface diffusion enhancement factor:

$$\frac{D_e}{D_b} - 1 = \frac{1 + \lambda}{w(\rho) + \lambda} \qquad (24)$$

where

$$w(\rho) = \frac{\tanh \rho}{\rho} \qquad (25)$$

$$\rho = \frac{1}{2}\left[\frac{\zeta(1 + K)^2 + 1}{K(1 + K)}\right]^{1/2} \qquad (26)$$

$$\lambda = \zeta \frac{(1 + K)^2}{K}. \qquad (27)$$

II. Slow Adsorption and Regular Perturbation Analysis for Small Φ

For small values of Φ, one can apply a different type of regular perturbation scheme, with X and θ expressed as

$$X(\xi) = X_0(\xi) + \Phi^2 X_1(\xi) + \Phi^4 X_2(\xi) + O(\Phi^8), \qquad (28)$$

$$\theta(\xi) = \theta_0(\xi) + \Phi^2 \theta_1(\xi) + \Phi^4 \theta_2(\xi) + O(\Phi^8). \qquad (29)$$

Expanding $G(X, \theta)$ around X_0, θ_0 in terms of Φ^2 and substituting (28)–(29) and the $G(X, \theta)$ expansion into Eqs. (8)–(12), one obtains for terms of order *zero:*

$$\frac{d^2X_0}{d\xi^2} = 0 \quad \text{and} \quad \frac{d^2\theta_0}{d\xi^2} = 0, \qquad (30)$$

$$\begin{aligned} X_0 &= 1; \quad \frac{d\theta_0}{d\xi} = 0 \quad \text{at } \xi = 0 \\ X_0 &= X_L; \quad \frac{d\theta_0}{d\xi} = 0 \quad \text{at } \xi = 1 \end{aligned} \qquad (31)$$

order *one:*

$$\frac{d^2X_1}{d\xi^2} = G(X_0, \theta_0) \qquad (32)$$

and

$$\frac{d^2\theta_1}{d\xi^2} = -\zeta G(X_0, \theta_0),$$

$$\begin{aligned} X_1 &= 0; \quad \frac{d\theta_1}{d\xi} = 0 \quad \text{at } \xi = 0 \\ X_1 &= 0; \quad \frac{d\theta_1}{d\xi} = 0 \quad \text{at } \xi = 1 \end{aligned} \qquad (33)$$

and, order *two:*

$$\begin{aligned} \frac{d^2X_2}{d\xi^2} &= G_X X_1 + G_\theta \theta_1 \\ \frac{d^2\theta_2}{d\xi^2} &= -\xi G_X X_1 - \zeta G_\theta \theta_1, \end{aligned} \qquad (34)$$

$$\begin{aligned} X_2 &= 0; \quad \frac{d\theta_2}{d\xi} = 0 \quad \text{at } \xi = 0 \\ X_2 &= 0; \quad \frac{d\theta_2}{d\xi} = 0 \quad \text{at } \xi = 1. \end{aligned} \tag{35}$$

The system of Eqs. (30)–(35) is again linear and admits analytical solutions. The mathematical details are similar to those in (*16*), and the resulting surface diffusion factor is found to be

$$\frac{D_e}{D_b} - 1 = -\Phi^2\left(\frac{\alpha_1}{1 - X_L}\right) - \Phi^4\left(\frac{\alpha_2}{1 - X_L}\right) + O(\Phi^8), \tag{36}$$

where

$$\alpha_1 = -\left[\frac{1 - X_L}{6[K(1 + X_L) + 2]}\right] \tag{37}$$

$$\begin{aligned} \alpha_2 = \frac{1}{180}&\left[\frac{1 - X_L}{[K(1 + X_L) + 2]^2}\right] + \frac{d_1}{12}\left[\frac{3(1 + K) - (1 - X_L)}{K}\right] \\ &- \frac{1}{40}\left[\frac{(1 + K)\zeta(1 - X_L)}{K[K(1 + X_L) + 2]}\right] + \frac{1}{72}\left[\frac{(1 - X_L)^2\zeta}{K[K(1 + X_L) + 2]}\right] \end{aligned} \tag{38}$$

with

$$\begin{aligned} d_1 = \frac{1}{6}&\left[\frac{(1 + K)\zeta(1 - X_L)}{[K(1 + X_L) + 2][(1 + X_L) + 2K]}\right] \\ &- \frac{7}{60}\left[\frac{(1 - X_L)^2\zeta}{[K(1 + X_L) + 2][1 + X_L + 2K]}\right] \end{aligned}$$

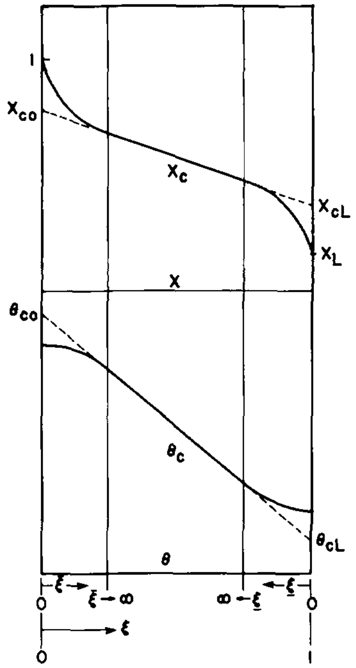

FIG. 1. Schematic of the boundary layer structure for the diffusion reaction problem described in Eqs. (8)–(12) for large values of Φ.

III. Rapid Adsorption and Singular Perturbation for Large Φ

Here we consider the case of rapid adsorption–desorption kinetics where one can employ a ("Kreuzer-Hoof'd") modified singular perturbation analysis discussed elsewhere (*12–14*). This provides a useful approximate solution, which becomes asymptotically exact in the equilibrium limit Φ → ∞. For large Φ (mathematically Φ → ∞), Eqs. (8)–(12) indicate a boundary layer structure depicted schematically in Fig. 1. In the central or "core" region of the pore

$$G(X, \theta) \simeq 0, \tag{39}$$

and therefore we obtain the adsorption–desorption equilibrium condition

$$\theta_c = \frac{KX_c}{1 + KX_c} \tag{40}$$

where θ_c and X_c are the core values of θ and X. At the left-hand boundary ($\xi = 0$), one introduces a new, stretched length coordinate

$$\bar{\xi} = \frac{\xi}{\varepsilon} \quad \text{with } \varepsilon = \frac{1}{\Phi} \to 0 \tag{41}$$

and assumes that

$$\begin{aligned} X = X_c + \varepsilon\bar{X}(\varepsilon, \bar{\xi}) &= X_c\Big|_{\xi=0} + \xi\left.\frac{dX_c}{d\xi}\right|_{\xi=0} + \varepsilon\bar{X}(\varepsilon, \bar{\xi}) \\ &= X_{c0} + \varepsilon\bar{\xi}\left.\frac{dX_c}{d\xi}\right|_{\xi=0} + \varepsilon\bar{X}(\varepsilon, \bar{\xi}) \end{aligned} \tag{42}$$

and

$$\theta = \theta_{c0} + \varepsilon\bar{\xi}\left.\frac{d\theta_c}{d\xi}\right|_{\xi=0} + \varepsilon\bar{\theta}(\varepsilon, \bar{\xi}). \quad (43)$$

Inserting Eqs. (41)–(43) into Eqs. (8)–(12) and also expanding $G(X, \theta)$ in terms of ε, we obtain the (vector) equations for the boundary layer profiles:

$$\begin{pmatrix} \bar{X} \\ \bar{\theta} \end{pmatrix}'' = \mathbf{M}\begin{pmatrix} \bar{X} \\ \bar{\theta} \end{pmatrix} \quad (44)$$

$$\bar{X} = \left(\frac{1 - X_{c0}}{\varepsilon}\right); \quad \frac{d\bar{\theta}}{d\bar{\xi}} = 0 \quad \text{at } \bar{\xi} = 0 \quad (45)$$

$$\bar{X} \to 0; \quad \bar{\theta} \to 0, \quad \text{as } \bar{\xi} \to \infty \quad (46)$$

where

$$(\ )'' = \frac{d^2}{d\bar{\xi}^2}(\ ) \quad (47)$$

and $\mathbf{M}$ is the (2×2) matrix of coefficients:

$$\mathbf{M} = \begin{bmatrix} \dfrac{\partial G}{\partial X} & \dfrac{\partial G}{\partial \theta} \\ -\zeta\dfrac{\partial G}{\partial X} & -\zeta\dfrac{\partial G}{\partial \theta} \end{bmatrix} = \begin{bmatrix} (1 - \theta_{c0}) & (X_{c0} + 1/K) \\ -\zeta(1 - \theta_{c0}) & \zeta(X_{c0} + 1/K) \end{bmatrix}. \quad (48)$$

The formal solution of Eqs. (44)–(46) is

$$\begin{pmatrix} \bar{X} \\ \bar{\theta} \end{pmatrix} = e^{-\bar{\xi}\mathbf{M}^{1/2}} \begin{bmatrix} \dfrac{1 - X_{c0}}{\varepsilon} \\ \bar{\theta}_0/\varepsilon \end{bmatrix} \quad (49)$$

where

$\bar{\theta}_0 = \bar{\theta}_{\bar{\xi}=0}$ (a value yet to be determined)

and

$$e^{-\bar{\xi}\mathbf{M}^{1/2}} = \left(\frac{e^{-\bar{\xi}t^{1/2}-1}}{t}\right)\mathbf{M} + \mathbf{I} \quad (50)$$

where

$$t = (1 - \theta_{c0}) + \zeta(X_{c0} + 1/K) = \frac{1}{1 + KX_{c0}} + \zeta\left(\frac{1 + KX_{c0}}{K}\right) \quad (51)$$

and $\mathbf{I}$ is the unit matrix.

The solution given in (49) satisfies the initial condition but in order to satisfy the boundary conditions at ∞, the following additional equation must be satisfied:

$$(\mathbf{I} - \mathbf{M}/t)\begin{pmatrix} 1 - X_{c0} \\ \bar{\theta}_0 \end{pmatrix} = 0, \quad (52)$$

from which one obtains

$$\bar{\theta}_0 = -\zeta(1 - X_{c0}). \quad (53)$$

The full solution of Eqs. (44)–(46) is then given by

$$\begin{pmatrix} \bar{X} \\ \bar{\theta} \end{pmatrix} = e^{-\bar{\xi}\mathbf{M}^{1/2}}\Phi(1 - X_{c0})\begin{bmatrix} 1 \\ -\zeta \end{bmatrix}. \quad (54)$$

One can apply a similar analysis at the right-hand boundary by defining a new stretched coordinate as

$$\underline{\xi} = \frac{1 - \xi}{\varepsilon}. \quad (55)$$

The solution in the right-hand boundary layer is given as

$$\begin{pmatrix} \underline{X} \\ \underline{\theta} \end{pmatrix} = e^{-(\mathbf{N}^{1/2}\underline{\xi})} \cdot \Phi(X_L - X_{cL})\begin{pmatrix} 1 \\ -\zeta \end{pmatrix}, \quad (56)$$

where

$$\mathbf{N} = \begin{bmatrix} 1 - \theta_{cL} & -(X_{cL} + 1/K) \\ -\zeta(1 - \theta_{cL}) & \zeta(X_{cL} + 1/K) \end{bmatrix}. \quad (57)$$

Certain matching conditions are now required. Since $d\theta/d\xi = 0$ at $\xi = 0$, transport into the pore can occur only by bulk diffusion. In the core region, however, transport occurs by combined bulk and surface diffusion. Since the system is nonreactive, these two fluxes must be equal, i.e.,

$$-\left.\frac{dX}{d\xi}\right|_{\xi=0} = -\frac{dX_c}{d\xi} - \zeta^{-1}\frac{d\theta_c}{d\xi} \quad (58)$$

which by means of Eq. (42) becomes

$$\left.\frac{d\bar{X}}{d\xi}\right|_{\xi=0} = \zeta^{-1}\frac{d\theta_c}{d\xi} = \zeta^{-1}(\theta_{cL} - \theta_{c0}) = \zeta^{-1}K\left[\frac{X_{cL}}{1 + KX_{cL}} - \frac{X_{c0}}{1 + KX_{c0}}\right]. \quad (59)$$

From Eqs. (54) and (59) one gets

$$\zeta(1 - X_{c0})t^{1/2}\Phi - K\left[\frac{X_{c0}}{1 + KX_{c0}} - \frac{X_{cL}}{1 + KX_{cL}}\right] = 0. \quad (60)$$

A similar equation can be derived for right-hand boundary:

$$-\zeta(X_L - X_{cL})t'^{1/2}\Phi - K\left[\frac{X_{c0}}{1 + KX_{c0}} - \frac{X_{cL}}{1 + KX_{cL}}\right] = 0 \quad (61)$$

where

$$t' = \frac{1}{1 + KX_{cL}} + \zeta\frac{(1 + KX_{cL})}{K}. \quad (62)$$

Equations (60)–(61) can be used to find the values for X_{c0} and X_{cL}. Once these are found, the enhancement factor is given by

$$\frac{D_e}{D_b} - 1 = \frac{(1 - X_{c0})[\Phi t^{1/2} - 1] + (X_L - X_{cL})}{1 - X_L} \quad (63)$$

which, incidentally, can be obtained from a general formula given in (*13*).

IV. The Equilibrium Limit

As mentioned in the Introduction, the oft-used assumption of complete adsorption equilibrium and the zero-flux conditions for the surface concentrations at the boundaries are intrinsically inconsistent. If instead one expresses the total diffusional flux as

$$-\pi r^2 D_b\frac{dC}{dx} - 2\pi r D_s\frac{dn}{dx} = \text{constant} \quad (64)$$

one obtains the effective diffusion equation

$$D_b\frac{d}{dx}\left[\left(1 + \frac{2}{r}\frac{D_s}{D_b}\frac{dn}{dC}\right)\frac{dC}{dx}\right] = 0 \quad (65)$$

where dn/dC is to be evaluated from the equilibrium condition (39). For the Langmuir type adsorption–desorption isotherm selected here the enhancement factor follows by integration, as

$$\frac{D_e}{D_b} - 1 = \zeta^{-1}\frac{K}{(1 + KX_L)(1 + K)}. \quad (66)$$

Both, the singular perturbation and Aris' regular perturbation expression ($X_L \simeq 1$) for the enhancement factor reduce to (66) for large values of the Thiele Modulus Φ. This is to be expected and serves as a consistency test for the two mathematical schemes.

NUMERICAL EXAMPLES

One should not expect Eqs. (24)–(27) and (66) to perform well outside the region of the parameter space for which intended. This is indicated in Figs. 2a–d, where the enhancement factor is plotted vs. Thiele Modulus for $\zeta = 0.1$, $K = 1$ and various values of $1 - X_L$. The enhancement factors derived from the above four approximate analytical expressions are compared with the exact value, derived by numerical solution of the system of Eqs. (8)–(12). The adsorption–desorption equilibrium expression performs very poorly in all four figures. The Aris expression works fairly well for large Φ in Fig. 2a ($1 - X_L = 0.01$) but rather poorly in the other cases, as was to be expected. Taken together, the perturbations in Φ, however, perform well. It is clear from Fig. 2 that an exact solution, such as that obtained from numerical solution of (8)–(12) is required only for a narrow region of X_L values. In the remaining range of Φ values, the two approximate solutions serve exceptionally well, which in our opinion, is very important for the field of surface diffusion. Since both expressions are analytical, they can be conveniently utilized in parameter identification and esti-

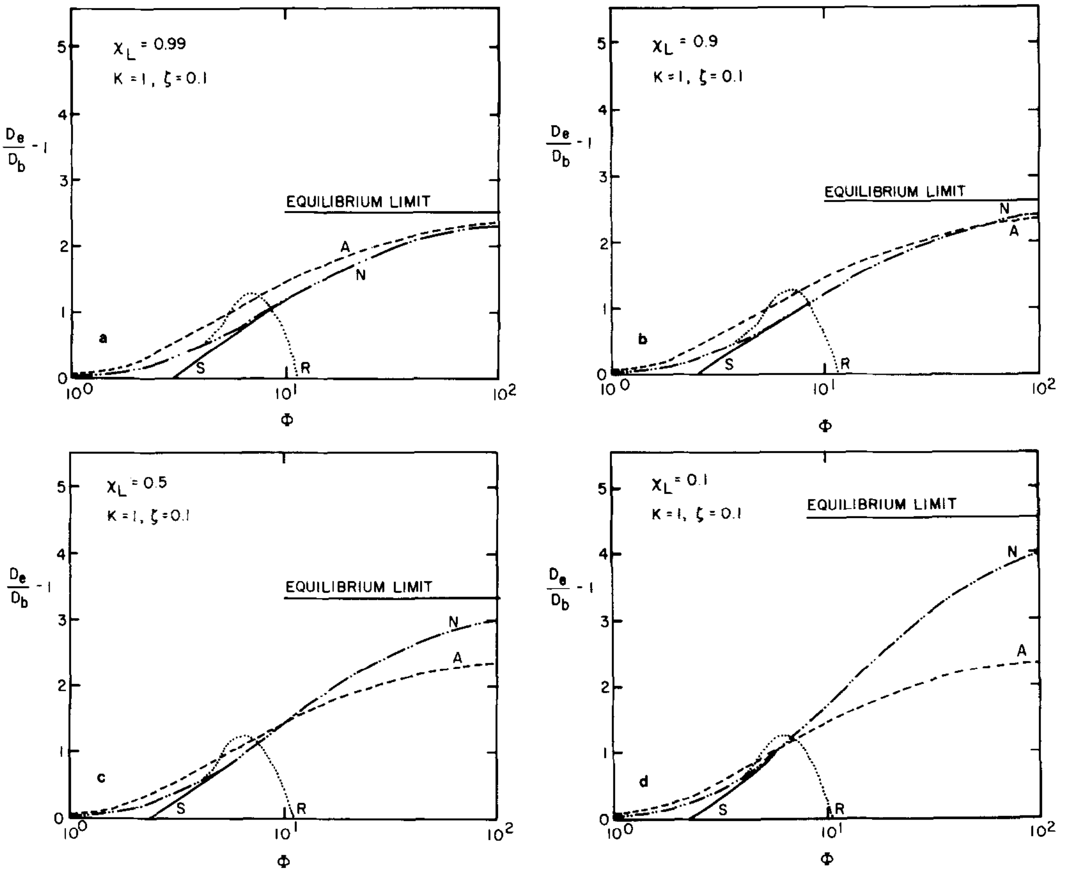

FIG. 2. Effect of Φ on the enhancement factor. (- - -) A, Aris linearized theory; (···) R, regular expansion for small Φ; (—·—·) N, numerical (exact) solution; (—) S, singular-perturbation approximate solution for large Φ (when different from N). (a) $X_L = 0.99$, $K = 1$, $\zeta = 0.1$. (b) $X_L = 0.9$, $K = 1$, $\zeta = 0.1$. (c) $X_L = 0.5$, $K = 1$, $\zeta = 0.1$. (d) $X_L = 0.1$, $K = 1$, $\zeta = 0.1$.

mation studies. Given the current state of parameter identification in distributed boundary-value problems, one readily appreciates the importance of such approximate analytical forms.

Table 1 shows the region of Φ values in which the two approximate solutions depart by more than 5% from the exact numerical result for different values of ζ and K. As can be seen, the agreement is outstanding. Figure 2 clearly point out that using adsorption equilibrium assumption may introduce serious errors in the interpretation of experimental data. We believe that all experimental surface diffusivities derived from this assumption should therefore be reevaluated.

To emphasize the above point and to show how serious the resulting errors are, the following "paper" experiment was performed. Using constant values of K, $1 - X_L$, and ζ and a region of Φ values (0–100), Eqs. (8)–(12) were numerically solved to calculate the corresponding enhancement factors. Using these enhancement factors and Eq. (66) the ζ values required to predict these factors were calculated. These calculated ζ^{-1} values (ζ^{-1} is proportional to D_s) are then compared with the original ζ^{-1} value and the resulting percent error is then plotted in Fig. 3 for different values of Φ.

As can be seen from Fig. 3, the adsorption equilibrium assumption can lead to serious underestimates of D_s. Figures 4 and 5

TABLE 1

Region of Φ Values for Different Values of ζ and K

	0.01	0.1	0.5	0.9
$\zeta = 0.1$ $K = 1$	1.5–4.8	1.5–4.8	1.6–4.6	1.7–4.4
$\zeta = 1$ $K = 1$	0.5–2.4	0.5–2.4	0.5–2.4	0.6–2.3
$\zeta = 10$ $K = 1$	0.2–0.7	0.2–0.7	0.2–0.8	0.2–0.8
$\zeta = 0.1$ $K = 0.1$	0.7–2.7	0.7–2.7	0.7–2.7	0.7–2.7
$\zeta = 0.1$ $K = 10$	2.0–8.7	2.0–8.7	2.5–8.3	2.5–8.3

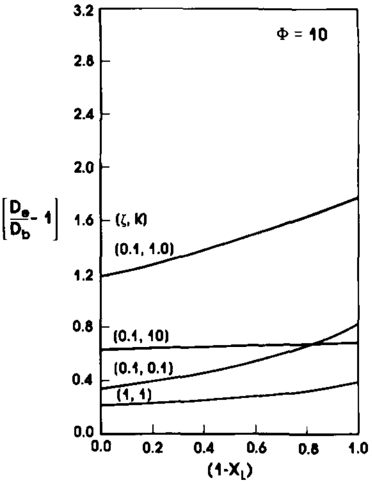

FIG. 4. Variation of enhancement factor as a function of $(1 - X_L)$ for various combinations of ζ and K; Φ = 10.

show enhancement factors vs $(1 - X_L)$ for different values of the other parameters. They qualitatively represent the trend of actual experimental data, which we now discuss.

SOME EXPERIMENTAL OBSERVATIONS

Figure 6 shows experimental data for effective diffusivity, generated in our experimental apparatus, shown schematically in Fig. 7. It contains a Pyrex-glass diffusion cell, consisting of two well-mixed half-cells separated by the membrane. The cell can operate in a batch–batch, CSTR–CSTR, or batch–CSTR mode. In the data presented here, the diffusing species is Ni-T3MPP porphyrin diffusing through a Nuclepore polycarbonate membrane with straight cylindrical pores of 300 Å in diameter and a thickness of 6 μm. To initiate the experiment, the bottom half-cell is filled with the desired concentration of Ni-T3MPP in mineral oil. Then the membrane is installed, the cell is assembled and the top half-cell is filled with pure mineral oil. The concentration gradient between the two well-mixed

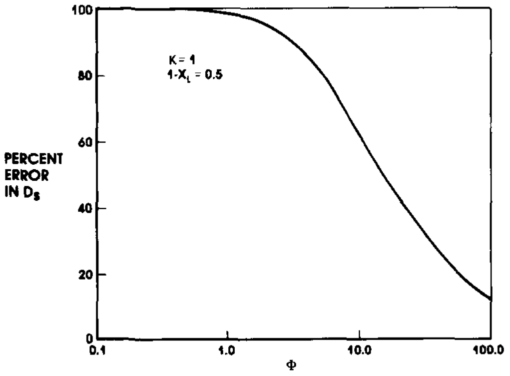

FIG. 3. Percentage error in D_s as a function of the Thiele Modulus (Φ).

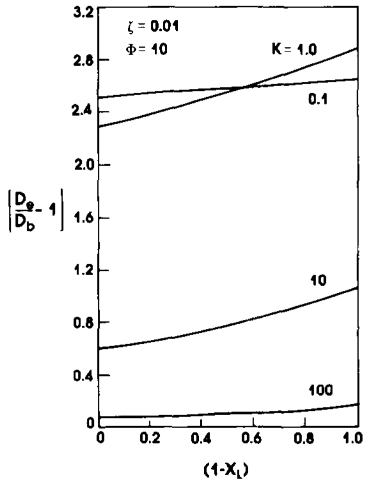

FIG. 5. Variation of enhancement factor as a function of $(1 - X_L)$ for various values of K; ζ = 0.01, Φ = 10.

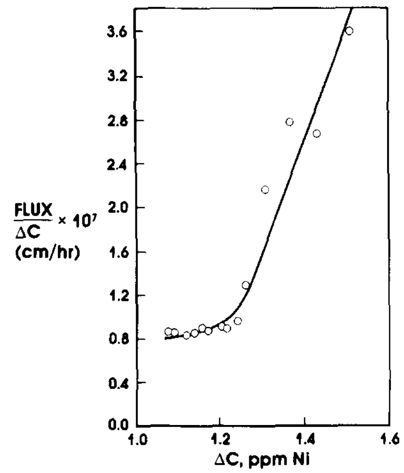

FIG. 6. Effect of concentration driving force on effective diffusivity for Ni-T3MPP at 25°C; membrane pore size 300 Å, membrane thickness 6 μm.

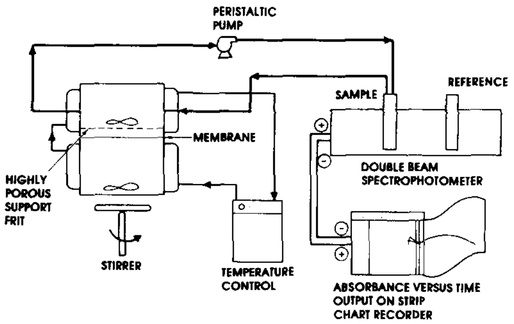

FIG. 7. Diffusion apparatus.

half-cells is continuously monitored by a double-beam UV spectrophotometer. One observes initially (for the first few hours) that the diffusional flux is a nonlinear function of the concentration difference in the half-cells, but at later times it becomes linear. This indicates that surface diffusion has ceased to be important, as is the case for small $1 - X_L$ in Figs. 4 and 5. Figure 8 shows similar behavior for another membrane of the same thickness (6 μm) with pore diameter of 150 Å.

CONCLUSIONS

The primary goal of the above study has been to clarify certain basic questions and outstanding problems in the field of surface diffusion in porous catalysts. Attention has been focused on various mathematical techniques for the analysis and interpretation of experimental data. The common assumption of adsorption equilibrium has been shown to lead to serious error (Fig. 3). It is clear, therefore, that most of the existing surface-diffusion data should be re-evaluated.

Two mathematical perturbation techniques, which have been presented, lead to analytical expressions for transport enhancement by surface diffusion, as a function of the relevant system parameters. Since these expressions appear to provide reliable prediction of overall diffusivities it is hoped that future work in the area will employ this relatively simple type of analysis to check the often erroneous assumption of adsorption equilibrium.

There remain a number of interesting questions in the field. Little is known about surface diffusion in the presence of surface and bulk chemical reactions or about the effect of complex pore structure (for exam-

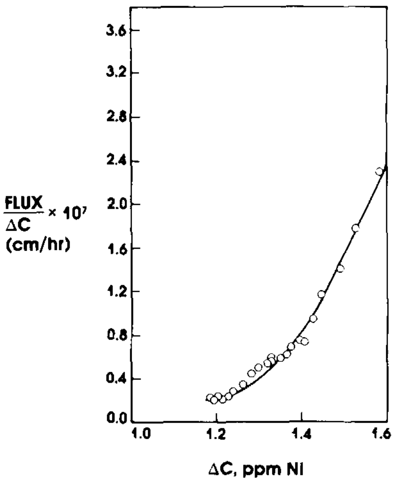

FIG. 8. Effect of concentration driving force on effective diffusivity for Ni-T3MPP at 25°C; membrane pore size 150 Å, membrane thickness 6 μm.

ple, are the surface and bulk tortuosity factors equal?). Also, the microscopic statistical aspects of surface diffusion need more study. It is not clear to us whether the commonly utilized Fickian forms are correct for diffusion in the presence of adsorption and surface inhomogeneities. Certain of these issues will be addressed in future works.

APPENDIX: NOMENCLATURE

a_v	surface to volume ratio; for a cylindrical pore $a_v = 2/r$
C	concentration of diffusing species in the pore
C_H	concentration at $x = 0$ (left pore boundary)
C_L	concentration at $x = L$ (right pore boundary)
D_b	bulk pore diffusivity
D_e	effective pore diffusivity, defined by Eq. (23)
D_s	surface diffusivity
$G(C, n)$	net rate of adsorption, defined by Eq. (7)
G_X, G_θ	partial derivatives of G, defined by Eq. (18)
$\mathbf{I}$	unit matrix
J_b	flux in the bulk of the pore
J_s	flux on the surface of the pore
K	dimensionless thermodynamic equilibrium constant
K_a	adsorption constant
K_d	desorption constant
L	pore length
$\mathbf{M}$	reaction matrix, defined by Eq. (48)
$\mathbf{N}$	reaction matrix defined by Eq. (57)
n	surface concentration in the pore
n_t	surface concentration at full coverage
r	pore radius
t	trace of matrix $\mathbf{M}$ defined by Eq. (51)
t'	trace of matrix $\mathbf{N}$ defined by Eq. (62)
x	length variable in the pore
X	dimensionless bulk concentration, C/C_H
X_c	dimensionless concentration in the core of the pore, used in the singular perturbation analysis
X_{c0}, X_{cL}	X_c at $\xi = 0$ and $\xi = 1$
$X_i(\xi)$	terms of the perturbation expansions, Eqs. (14) and (30)

Greek Symbols

ε	parameter used in regular and singular perturbation analysis
ζ	$(C_H D_b)/(n_t a_v D_s)$
θ	dimensionless surface concentration, n/n_t
θ_c	value of θ in the core of the pore, used in singular perturbation analysis
θ_{c0}, θ_{cL}	θ_c at $\xi = 0$, $\xi = 1$
$\theta_i(\xi)$	terms of perturbation expansions, Eqs. (15) and (31)
$\bar{\theta}(\varepsilon, \bar{\xi})$	terms in the singular perturbation analysis
λ	$\zeta(1 + K)^2/K$
ξ	x/L
ρ	$\frac{1}{2}[(\zeta(1 + K)^2 + 1)/K(1 + K)]^{1/2}$
Φ	$L[K_a n_t C_H/D_b]^{1/2}$

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