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Manuscript received June 16, 1981; revision received June 28, 1983; and accepted Aug. 24.

A Correction Factor for Mass Transfer Coefficients for Transport to Partially Impenetrable or Nonadsorbing Surfaces

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INTRODUCTION

Most correlations for liquid-solid mass transfer coefficients in packed or fluidized beds or for surfaces having other various geometries are based primarily upon measurement of dissolution rates using soluble packings (Evans and Gerald, 1953; Goto and Smith, 1975; Goto et al., 1975; Hirose et al., 1976; Kataoka et al., 1972; Lemay et al., 1975; Specchia et al., 1976, 1978; Sylvester and Pitayagusarn, 1975; Van Krevelen and Krekels, 1948; Wilson and Geankopolis, 1966). Other techniques that have been used to a lesser extent include those based upon electrochemical methods (Colquhoun-Lee and Stepanek, 1978; Karabelas et al., 1971), tracer methods (Tan and Smith, 1982), or adsorption using a chemical reaction in the mass transfer controlled regime (Snider and Perona, 1974). Critical reviews and a summary of the significant findings are available (Charpentier, 1976, 1981; Karabelas et al., 1971; Dwivedi and Upadhyay, 1977; Wakao and Funazkri, 1978). Care is usually taken to ensure that the solid surfaces used are smooth on the scale of the boundary layer thickness so that the actual interfacial area available for transport corresponds to the geometric area on which the calculated mass transfer coefficients are based. These mass transfer coefficients obtained are essentially for nonporous solid surfaces and are often used to predict mass fluxes in systems where only a fraction of the external area of the solid participates in the transport. Such is the case of a discretely dispersed catalyst on a nonadsorbing, nonporous support or the case of porous catalysts. Common engineering practice is to base the mass transfer coefficients on the total external area. The question then arises whether the mass transfer coefficient obtained in systems where total external area participates in transport, k^o_{mt}, should be modified for the case where the transport occurs only to a fraction f of the external area but the coefficient k_{mt} is still based on the total area. Conventional wisdom (Herskowitz et al., 1979) suggests that the two are related by:

$$k_{mt} = f\,k^o_{mt} \tag{1}$$

Equation 1 implies that if the mass transfer coefficients are based per unit active area available for transport, they would be unchanged irrespective of whether the whole surface or only part of it is active in the transport process. This would suggest that the following equality be satisfied:

$$k^o_{ma} = k^o_{mt} = k_{ma} = \frac{k_{mt}}{f} \tag{2}$$

where k_{ma} is the mass transfer coefficient for a partially active surface based per unit area of active surface. Our objective is to test this hypothesis based on a simple two-dimensional model for mass transfer to a solid surface.

MODEL

We consider here the simplest two-dimensional situation of transport by diffusion through a boundary layer of constant thickness δ to a nonuniform surface as shown in Figure 1. The surface is nonuniform in the sense that it has periodically distributed active and inactive areas. The half-width of the active area is denoted here by p and the half-width of the inactive area by $(w - p)$. By placing the origin of the coordinate system at the center of an active area, the lines of symmetry are located at $x = 0$ and $x = w$.

The active areas may represent pore mouths or active catalyst crystallites. We assume that the bulk fluid at $y = \delta$ is maintained at a constant concentration of the diffusing species $c = c_b$. The active area of the surface at $y = 0$ for $0 \le x < p$ exists at some finite

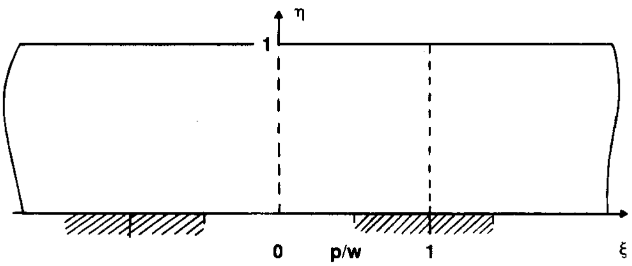

Figure 1. Diffusion to a partially impenetrable surface.

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solute concentration denoted here by $c = c_s$, while the inactive portion of the solid surface; i.e., the portion $p < x \le w$, is impermeable to the solute so that $\partial c/\partial y = 0$. The governing equations and boundary conditions in dimensionless form can be summarized as:

$$\left(\frac{\delta}{w}\right)^2 \frac{\partial^2 u}{\partial \xi^2} + \frac{\partial^2 u}{\partial \eta^2} = 0 \tag{3}$$

$$\xi = 0, \quad \frac{\partial u}{\partial \xi} = 0; \quad 0 \le \eta \le 1 \tag{4}$$

$$\xi = 1, \quad \frac{\partial u}{\partial \xi} = 0; \quad 0 \le \eta \le 1 \tag{5}$$

$$\eta = 0 \quad \begin{cases} u = 0; \quad 0 \le \xi < \xi_o & \text{(6a)} \\ \dfrac{\partial u}{\partial \eta} = 0; \quad \xi_o < \xi \le 1 & \text{(6b)} \end{cases}$$

$$\eta = 1, \quad u = 1; \quad 0 \le \xi \le 1 \tag{7}$$

Here, $u = (c - c_s)/(c_b - c_s)$ is the normalized solute concentration while $\xi = x/w$ and $\eta = y/\delta$ are the dimensionless coordinates. The point where the discontinuity in the boundary condition at the solid surface occurs is denoted by $\xi_o = p/w$.

We have shown elsewhere (Mills and Duduković, 1980; 1982; 1983) what techniques could be used to solve boundary value problems with discontinuous boundary conditions of which the above one is an example. An analytical solution that satisfies Eqs. 3–5 and Eq. 7 is:

$$u(\xi,\eta) = \eta + a_o \frac{\delta}{w}(1 - \eta) + \sum_{n=1}^{\infty} a_n \frac{\sinh\left(\dfrac{n\pi\delta}{w}(1-\eta)\right)}{n\pi \cosh\left(\dfrac{n\pi\delta}{w}\right)} \cos(n\pi\xi) \tag{8}$$

The unknown coefficients a_n are obtained by forcing Eq. 8 to satisfy the remaining boundary conditions given by Eq. 6. This results in the following dual series equations for the coefficients a_n:

$$a_o \frac{\delta}{w} + \sum_{n=1}^{\infty} a_n \frac{\tanh\left(n\pi\dfrac{\delta}{w}\right)}{n\pi} \cos(n\pi\xi) = 0; \quad 0 \le \xi < \xi_o \tag{9a}$$

$$a_o + \sum_{n=1}^{\infty} a_n \cos(n\pi\xi) = \frac{w}{\delta}; \quad \xi_o < \xi \le 1 \tag{9b}$$

The mass transfer coefficient for diffusion through a layer of constant thickness δ to a uniformly accessible surface (i.e., total active surface with $p = w$) is:

$$k^o_{mt} = D/\delta \tag{10}$$

The mass transfer coefficient correction factor is then obtained by

$$\alpha = \frac{k_{mt}}{k^o_{mt}} = \frac{D \displaystyle\int_0^w \frac{\partial c}{\partial y}\bigg|_{y=\delta} \frac{dx}{w}}{(D/\delta)(c_b - c_s)} = \int_0^1 \frac{\partial u}{\partial \eta}\bigg|_{\eta=1} d\xi \tag{11}$$

Performing the operation indicated by Eq. 11 using Eq. 8 shows that the correction factor is given in terms of the leading dual series coefficient a_o by the following expression:

$$\alpha = 1 - a_o \frac{\delta}{w} \tag{12}$$

From Eqs. 12 and 9, it is clear that the correction factor is a function of two aspect ratio parameters: δ/w and p/w. We can readily obtain the value of a_o using the software package DTRIGS that was developed for the rapid solution of dual trigonometric series problems by the method of weighted residuals (Mills and Duduković, 1980, 1982). However, another accurate solution can be obtained with much less computational effort if the above set of dual-series equations is reduced to the following integral equation for the unknown function $g(\xi)$ (Mills and Duduković, 1983):

$$\int_0^{\xi_o} K(\xi,\xi')g(\xi)d\xi = F(\xi') \tag{13}$$

where:

$$K(\xi,\xi') = \frac{\delta}{w}\frac{1}{\pi} ln\, 2 - \frac{1}{\pi} ln\left|\cos(\pi\xi) - \cos(\pi\xi')\right| + 2\sum_{n=1}^{\infty} \frac{\tanh\left(\dfrac{n\pi\delta}{w}\right) - 1}{n\pi} \cos(n\pi\xi)\cos(n\pi\xi') \tag{14}$$

$$F(\xi') = \xi_o - 1 + 2\sum_{n=1}^{\infty} \frac{\tanh(n\pi\delta/w)}{(n\pi)^2\delta/w} \sin(n\pi\xi_o)\cos(n\pi\xi') \tag{15}$$

In this case, $g(\xi)$ is equal to the series defined by Eq. 9b when this series is continued into the interval $0 \le \xi < \xi_o$. The leading coefficient a_o necessary for evaluation of the correction factor by Eq. 12 is now given by:

$$a_o = \int_0^{\xi_o} g(\xi)d\xi + \frac{w}{\delta}(1 - \xi_o) \tag{16}$$

We have shown (Mills and Duduković, 1983) that an accurate solution to an equivalent form of Eq. 13 obtained by introducing the stretching coordinate $\omega = \xi/\xi_o$ is possible using as few as $N = 4$ Gaussian quadrature points. Using the calculated values $g(\omega_j\xi_o)$ at the quadrature points, evaluating the integral in Eq. 16 by Gaussian quadrature, and substitution of Eq. 16 into Eq. 12 eventually yields the following expression for the correction factor α:

$$\alpha = \left(\frac{p}{w}\right)\left[1 - \left(\frac{\delta}{w}\right)\sum_{j=1}^{N} w_j g(\omega_j\xi_o)\right] \tag{17}$$

where w_j are the appropriate Gaussian weights.

DISCUSSION AND CONCLUSIONS

The calculated values of the correction factor are presented as a function of p/w with δ/w as a parameter in Figure 2, and as a function of δ/w with p/w as a parameter in Figure 3. Examination of these figures readily reveals that the "truism" expressed by Eq. 1, which is represented by a diagonal line in Figure 2, is approached *only* when $\delta/w < 0.1$. Apparently, at small δ/w, the flux lines do not have sufficient distances to "bend" and reach the active surface so that continuity results in a reduction of the flux to the surface.

Typical ranges for the characteristic length scale p of catalytic crystallites are 10–100 Å and for catalytic pore mouths are 10^3 to 10^5 Å. It is highly unlikely that the condition $\delta/w \ll 1$ will be satisfied when either one of these ranges are used for comparison to the typical boundary-layer thickness δ. A possible exception to this

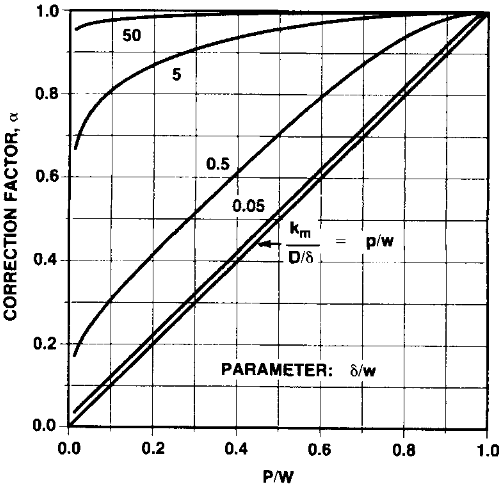

Figure 2. Mass transfer coefficient correction factor as a function of the fractional area available for diffusion *p/w*.

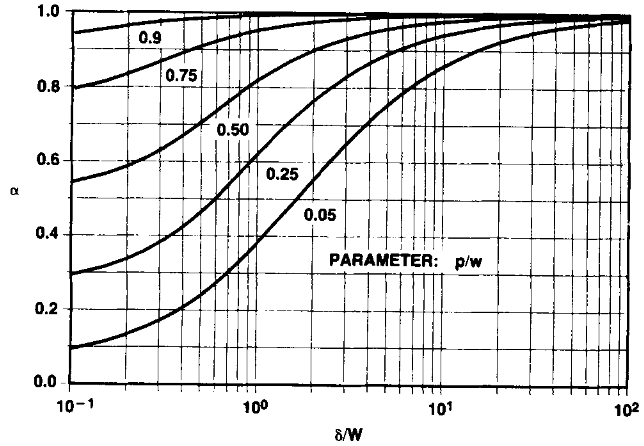

Figure 3. Mass transfer coefficient correction factor as a function of the aspect ratio δ/w.

would be the case where the catalyst crystallites or pore mouths are very sparsely distributed so that $w > 10^6$ Å.

At the other extreme when $\delta/w \gg 1$, i.e., the boundary layer thickness δ is much larger than the characteristic length w for dispersion of active catalyst in the surface, Eqs. 1 and 2 do not hold at all. The mass transfer coefficient is unaffected by changes in the aspect ratio p/w except at very low p/w values. Under these conditions, the flux lines do not have to bend as severely and the flux at the active surface is augmented.

In conclusion, the two dimensional model predicts the following relationships between mass transfer coefficients on fragmentary and uniformly active surfaces:

$$\text{For } \frac{\delta}{w} < 0.1, \quad \frac{k_{mt}}{k^o_{mt}} = \frac{p}{w}; \quad \frac{k_{ma}}{k^o_{ma}} = 1 \tag{18a}$$

$$\text{For } \frac{\delta}{w} > 100, \quad \frac{p}{w} > 0.1, \quad \frac{k_{mt}}{k^o_{mt}} = 1; \quad \frac{k_{ma}}{k^{om}_{a}} = \frac{w}{p} \tag{18b}$$

For $0.1 < \delta/w < 100$, Figures 2 and 3 should be consulted. This simple analysis indicates that caution should be exercised in applying Equations 1 or 2 when correcting mass transfer coefficients for partially active surfaces.

ACKNOWLEDGMENT

M. P. Duduković is grateful to UCLA for providing ample time to finish this manuscript.

NOTATION

a_n = dual series coefficients
c = concentration of the diffusing species, kmol/m^3
c_b = concentration of the diffusing species in the bulk, kmol/m^3
c_s = concentration of the diffusing species on the catalyst surface
D = diffusivity of the diffusing species, m^2/s
F = function defined by Eq. 15
f = fraction of surface that is active for transport
g = unknown function in the integral Eq. 13
K = kernel of the integral equation defined by Eq. 14
k_{ma} = mass transfer coefficient on the partially active surface based per unit active surface, m/s
$k^o_{ma} = k^o_{mt} = D/\delta$ = mass transfer coefficient on a uniformly or completely active surface based per unit surface, m/s
k_{mt} = mass transfer coefficient on the partially active surface based per unit area of total surface, m/s
N = total number of quadrature points
p = half width of active surface, m
$u = (c - c_s)/(c_b - c_s)$ = dimensionless concentration of the diffusing species
w_j = Gaussian quadrature weight factors
w = half distance between two active surface patches, m
x = coordinate along the surface, m
y = coordinate perpendicular to the surface, m

Greek Letters

$\alpha = k_{mt}/k^o_{mt}$ = correction factor for mass transfer coefficients defined by Eq. 11
δ = boundary layer thickness, m
$\eta = y/\delta$ = dimensionless coordinate perpendicular to the surface
$\xi = x/w$ = dimensionless coordinate along the surface
$\xi_o = p/w = f$ = dimensionless position of surface boundary condition discontinuity and dimensionless fraction of surface that is active for transport
$\omega = \xi/\xi_o$ = stretched coordinate, dimensionless

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Manuscript received Dec. 15, 1983; revision received Feb. 21, 1984, and accepted Mar. 1.

Effect of Pressure and Temperature on Restrictive Diffusion of Solutes in Aluminas

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PREVIOUS STUDIES

Previous studies of the diffusion of molecules in porous solids have been recently reviewed (Chantong, 1982). These studies have shown that when the critical molecular diameter of the diffusing molecule is an appreciable fraction of the pore diameter of the solid, diffusion is retarded from that of normal pore diffusion. The phenomenon has been termed "restrictive diffusion" and has been explained on the basis of steric hindrance and hydrodynamical drag effects.

On the basis of diffusion measurements of various molecules in silica-alumina beads, Satterfield et al. (1973) have derived an empirical equation relating the critical molecular diameter to pore diameter, λ, as:

$$F(\lambda) = \frac{D_e \tau}{D_b \epsilon} = e^{-4.6\lambda}$$

Later studies by Chantong and Massoth (1983) with polyaromatic compounds in aluminas gave a similar relationship, *viz.*,

$$F(\lambda) = \frac{D_e \tau_o}{D_b} = 1.03\, e^{-4.5\lambda}$$

confirming the general validity of this form for adsorbing and nonadsorbing solutes. In this study, we report data on the effects of pressure and temperature on the restrictive factor.

EXPERIMENTAL

Three different aluminas were used, having average pore diameters: C-15.4 nm, M-7.2 nm, and L-4.9 nm. Other physical properties of the aluminas are given by Chantong and Massoth (1983). The aluminas were crushed and sieved to give fractions among 0.417–0.701 mm, 0.208–0.417 mm, and 0.104–0.208 mm. The arithmetic average of the two values was taken as the particle diameters. Coronene (Aldrich), octaethylporphyrin (Man-Win), and tetraphenylporphyrin (Aldrich) were used as adsorbates. Their critical diameters are: 1.11 nm, 1.53 nm and 1.9 nm, respectively. n-Dodecane (Aldrich, 99%) was employed as solvent for higher temperature runs because of its low vapor pressure, and n-decane (Aldrich, 99+%) and cyclohexane (Matheson, Coleman and Bell, spectrograde) were used in the high pressure experiments at ambient temperature. All solvents were treated with calcined molecular sieve to remove water and other impurities.

A 1-L packless autoclave with Magnedrive assembly was used for the diffusion studies. A known weight of alumina, calcined at 773 K for 18 hours, was rapidly transferred to a fine-mesh stainless steel gauze basket and the basket immediately immersed into the solvent in order to prevent moisture pickup. A solution of known concentration of the aromatic compound in 500 cm^3 was prepared and transferred to the autoclave. The stirrer was then turned on and operated at 600 rpm. Above 500 rpm, measured diffusivities were not affected by stirring speed (Chantong, 1982). Molecular sieve 5A (~0.5 g), calcined at 523 K for 4 hours, was added to the solution and stirred at the given temperature for overnight to remove interfering materials.

At a given starting time, the basket containing the alumina was removed from the solvent and placed in the solution in the reactor. Samples (2 cm^3) were taken periodically and analyzed using a Beckman Model 25 UV-VIS spectrometer at 328.8 nm for coronene, at 498.7 nm for octaethylporphyrin and at 512.4 nm for tetraphenylporphyrin. As there was an appearance of chemical reaction of tetraphenylporphyrin at 363 K during the diffusion experiment, the upper temperature was confined to 333 K.

Effective diffusivities were determined from the uptake data by applying a pore diffusion model described previously (Chantong and Massoth, 1983). However, since reproducible isotherms at elevated temperatures could not be obtained, a linear isotherm was used in all diffusivity calculations.

RESULTS AND DISCUSSION

No significant effect of helium pressure on effective diffusivities of the solutes was observed at 7.0 MPa. There was also no difference

TABLE 1. EFFECT OF H_2 PRESSURE ON EFFECTIVE DIFFUSIVITIES OF CORONENE IN ALUMINA C AND L AT 298 K

	D_e, cm^2/s					
Alumina	C		C		L	
Solvent	n-decane		cyclohexane		cyclohexane	
Pres., MPa	0.29	7.0	0.085	7.0	0.29	7.0
$D_e \times 10^6$, cm^2/s	4.9	4.7	4.1	4.3	3.8	3.7

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