where the Sherwood number N_{Sh} can be related to the flowing stream by any one of a number of standard correlations. In addition, our formulae can be extended to include radiation and intraparticle transport with the same ease as Spalding's formulae.

In summary, it has been shown that (1) Spalding's model is equivalent to ours at an intermediate state, (2) our final formulation is more amenable to analysis than Spalding's and (3) the advantages which Mills attributes to Spalding's formulation are realized by our formulation as well.

NOTATION

See Newbold and Amundson (1973) as well as Mills' notation.

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A Model for the Application of Gas Chromatography to Measurements of Diffusion in Bidisperse Structured Catalysts

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In a recent article, Ma and Mancel (1972) reported the results of their investigation of the diffusion of gases in zeolites by the gas chromatography (GC) technique. They discuss the fact that the effective diffusivity derived from their results is due to some combination of contributions from macropore and micropore diffusion terms. The precise manner in which these two diffusion terms combine, however, is not known. This is because the theory of transient behavior of chromatograph columns developed originally by van Deemter et al. (1956) and extended and improved by Suzuki and Smith (1971) is applicable only to catalysts possessing a unimodal pore size distribution.

This note describes a model of transient diffusion in a GC column which we believe to be applicable to bidisperse structured catalyst particles, that is, particles characterized by two peaks in the distribution of pore sizes. The model does not require that the peaks be sharply defined. A bidisperse structured catalyst may be formed by compressing, extruding, or in some other manner compacting finely powdered microporous material into a pellet. Ideally the micropores are due to porosity inherent in the individual microparticles of catalyst. The macropores result from voids between the microparticles after pelletization or extrusion.

THE MODEL

A single effective diffusion coefficient cannot adequately characterize the mass transfer within a bidisperse structured catalyst when the contributions from both pore systems are substantial. In a realistic model the separate identity of the macropore and micropore structures must be maintained, and the diffusion must be described in terms of two coefficients, an effective macropore diffusivity, and an effective micropore diffusivity. Mingle and Smith (1961) and Carberry (1962) employed such a macro-micro-pore model in their evaluation of effectiveness factors in bidisperse structured catalysts. More recently Rukenstein et al. (1971) used the macro-micro-pore model in their study of sorption rates of gases and vapors in ion exchange resins. The model as applied to the GC effective diffusivity experiment is illustrated in Figure 1. This model might be expected to apply when the diffusivity in the micropores or microparticles D_x is considerably smaller than the macropore diffusivity D_y for only in this circumstance can the microparticle contribution to the radial flux in the catalyst particle be neglected. In our development we have employed a moments analysis to this model of pore structure to obtain an equation relating quantities extracted from the chromatogram to the model parameters.

A mass balance on the diffusing species across a differential element of microparticle results in the following partial differential equation with boundary conditions:

$$\frac{\partial^2 C_x}{\partial x^2} + \frac{2}{x}\,\frac{\partial C_x}{\partial x} = \frac{\theta_x}{D_x}\,(1 + K_a)\,\frac{\partial C_x}{\partial t} \qquad (1)$$

$$C_x(R_x, t) = C_y(y, t) \qquad (2)$$

$$\frac{\partial C_x}{\partial x}(0,t) = 0 \tag{3}$$

$$C_x(x,0) = 0 \tag{4}$$

In deriving Equation (1) it was assumed that adsorption is instantaneous and reversible and that the isotherm is linear. The dimensionless adsorption constant K_a is defined by Equation (5):

$$K_a = \frac{\rho S_x}{\theta_x(1-\theta_y)} \frac{C_a}{C_x} \tag{5}$$

In general, the linearity assumption is reasonable when concentrations are sufficiently low that surface coverage of the diffusing component is only a few percent of a monolayer. Schneider and Smith (1968a) point out that slightly higher inlet pulse concentrations may be tolerated due to the rapid decline in pulse concentration once the pulse enters the column. Another paper by these same authors (Schneider and Smith, 1968b) describes a method by which surface diffusion may be included in the calculations.

In view of the low macropore surface areas characteristic of most heterogeneous catalysts, adsorption in the macropores will be neglected. A mass balance across an element of catalyst particle gives

$$\frac{\partial^2 C_y}{\partial y^2} + \frac{2}{y}\frac{\partial C_y}{\partial y} + \frac{3(1-\theta_y)}{R_x D_y} N_{Rx} = \frac{\theta_y}{D_y}\frac{\partial C_y}{\partial t} \tag{6}$$

$$C_y(R_y, t) = C_z(z,t) + \frac{1}{k_f} N_{Ry} \tag{7}$$

$$\frac{\partial C_y}{\partial y}(0,t) = 0 \tag{8}$$

$$C_y(y,0) = 0 \tag{9}$$

where

$$N_{Rx} = -D_x \frac{\partial C_x}{\partial x}\bigg|_{Rx} \tag{10}$$

Writing a mass balance across a differential element of column length;

$$\frac{\partial^2 C_z}{\partial z^2} - \frac{v}{D_z}\frac{\partial C_z}{\partial z} + \frac{3(1-\theta_z)}{R_y D_z} N_{Ry} = \frac{\theta_z}{D_z}\frac{\partial C_z}{\partial t} \tag{11}$$

$$C_z(0, 0<t<\tau) = C_0 \quad (=0, \text{ otherwise}) \tag{12}$$

$$C_z(\infty, t) = 0 \tag{13}$$

$$C_z(z,0) = 0 \tag{14}$$

and

$$N_{Ry} = -D_y \frac{\partial C_y}{\partial y}\bigg|_{Ry} \tag{15}$$

This system of equations describes the time response of the column to the square wave input defined by Equation (12). The boundary conditions, Equations (12) and (13), are chosen as an alternative to the more accurate, but relatively complex, Danckwerts limits. In similar problems this approximation has proven valid when D_z is small (Smith, 1970). Any deviations from plug flow in the column are assumed to be adequately described by the axial dispersion model. The mass transfer parameters are (1) the axial dispersion coefficient D_z, (2) the external mass transfer coefficient k_f, (3) the effective macropore diffusivity D_y, and (4) the effective micropore diffusivity D_x.

The solution of the set of Equations (1) to (15) has not been attempted. Instead the mean μ and the variance about the mean σ^2 of the tracer distribution at the outlet of the column have been obtained. It is recalled that the defining equations for μ and σ^2 are

$$\mu = \frac{\int_0^\infty t C_L(t)\,dt}{\int_0^\infty C_L(t)\,dt} \tag{16}$$

$$\sigma^2 = \frac{\int_0^\infty (t-\mu)^2 C_L(t)\,dt}{\int_0^\infty C_L(t)\,dt} \tag{17}$$

Since the same method employed by others (for example, Suzuki and Smith, 1971) was used to obtain relations between μ, σ^2 and the mass transfer parameters, the details will be omitted.[*] Briefly the procedure involves transforming Equations (1), (6) and (11) into the Laplace domain with respect to t and solving the resulting ordinary differential equations with the transformed boundary conditions. The moments

$$m_n = \int_0^\infty t^n C_L(t)\,dt \tag{18}$$

of the chromatogram (easily related to μ and σ^2) were then obtained from the expression (Levenspiel and Bischoff, 1963)

$$m_n = (-1)^n \operatorname*{Limit}_{s\to 0} \frac{d^n \tilde{C}_L}{ds^n} \tag{19}$$

The results are

$$\mu = \frac{\tau}{2} + \frac{L}{v}[\theta_z + (1-\theta_z)\theta_y + (1-\theta_z)(1-\theta_y)\theta_x(1+K_a)] \tag{20}$$

$$\sigma^2 = \frac{\tau^2}{12} + \frac{2LD_z}{v^3}[\theta_z + (1-\theta_z)\theta_y$$

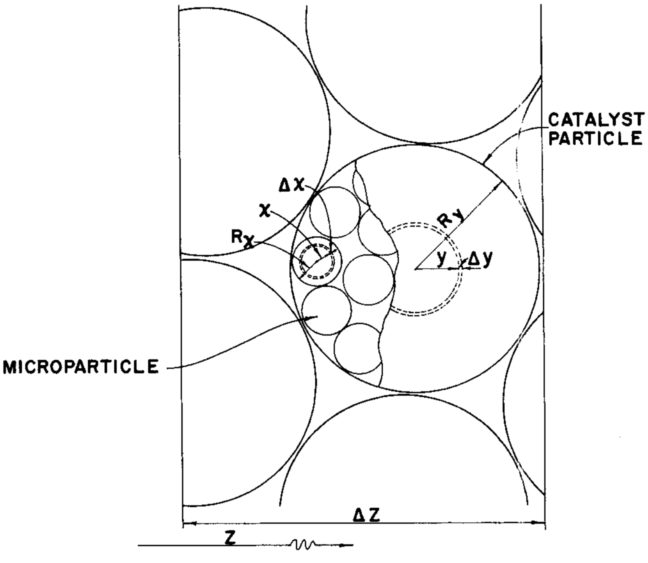

Fig. 1. Macro-micro-pore model.

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[*] Supplementary material has been deposited as Document No. 02092 with the National Auxiliary Publications Service (NAPS), c/o Microfiche Publications, 305 E. 46 St., New York, N. Y. 10017 and may be obtained for $1.50 for microfiche or $2.00 for photocopies.

$$+ (1 - \theta_z)(1 - \theta_y)\,\theta_x\,(1 + K_a)]^2$$

$$+ \frac{2L(1 - \theta_z)\,[\theta_y + (1 - \theta_y)\,\theta_x\,(1 + K_a)]^2 R_y}{3vk_f}$$

$$+ \frac{2L(1 - \theta_z)\,[\theta_y + (1 - \theta_y)\,\theta_x\,(1 + K_a)]^2 R_y^2}{15vD_y}$$

$$+ \frac{2L(1 - \theta_z)(1 - \theta_y)\,\theta_x^2\,(1 + K_a)^2\,R_x^2}{15vD_x} \qquad (21)$$

Thus the variance of the tracer function exiting the column is separable into contributions from each of the transport parameters D_z, k_f, D_y, and D_x.

It is of interest to compare these results with the results for a catalyst characterized by a unidisperse pore structure. Upon setting $\theta_x = 0$, $\theta_y = \theta =$ total porosity, and $D_y = D =$ "combined" effective diffusivity, Equations (20) and (21) reduce to

$$\mu = \frac{\tau}{2} + \frac{L}{v}\,[\theta_z + (1 - \theta_z)\,\theta] \qquad (22)$$

$$\sigma^2 = \frac{\tau^2}{12} + \frac{2LD_z}{v^3}\,[\theta_z + (1 - \theta_z)\,\theta]^2$$

$$+ \frac{2L(1 - \theta_z)\,\theta^2\,R_y}{3vk_f} + \frac{2L(1 - \theta_z)\,\theta^2\,R_y^2}{15vD} \qquad (23)$$

Equations (22) and (23) are identical with the results derived by Suzuki and Smith (1971) for the case of diffusion of a nonadsorbed gas in a bed of unidisperse structured catalyst particles. (The adsorption term does not appear in these equations because we earlier neglected adsorption in the macropores.) If a correction for adsorption is introduced into Equations (22) and (23), then the resulting equations are the equations presently used in the calculation of GC effective diffusivities.

Often it is convenient to employ an impulse input to the column instead of the square wave input of Equation (12). In this situation Equations (20) and (21) (with $\tau = 0$) are still applicable. It is sometimes convenient to describe peak broadening in terms of plate height:

$$H = \frac{\sigma^2}{\mu^2}\,L \qquad (24)$$

Substituting from Equations (20) and (21)

$$H = \frac{2D_z}{v} + Cv \qquad (25)$$

where

$$C = \frac{\dfrac{2(1 - \theta_z)\,[\theta_y + (1 - \theta_y)\,\theta_x\,(1 + K_a)]^2 R_y}{3k_f} + \dfrac{2(1 - \theta_z)\,[\theta_y + (1 - \theta_y)\,\theta_x\,(1 + K_a)]^2 R_y^2}{15D_y} + \dfrac{2(1 - \theta_z)(1 - \theta_y)\,\theta_x^2\,(1 + K_a)^2 R_x^2}{15D_x}}{[\theta_z + (1 - \theta_z)\,\theta_y + (1 - \theta_z)(1 - \theta_y)\,\theta_x\,(1 + K_a)]^2} \qquad (26)$$

Equation (25) can be put in the same form as the well-known result of van Deemter, et al. (1956) if it is assumed that the molecular and eddy diffusion contributions to D_z are additive. Then

$$H = A + \frac{B}{v} + Cv \qquad (27)$$

where $A = 2l$ and $B = 2\eta\,D_{AB}$. Procedures for estimating the molecular diffusibility η, and the scale of dispersion l are available in a recent publication by Suzuki and Smith (1972). The C parameter of Equation (26) is similar to that of van Deemter but contains the additional term due to D_x. Other relatively minor differences between the two expressions are due to approximations in the earlier theory as discussed by Davis and Scott (1965, 1968).

DISCUSSION

Of particular importance in experiments with bidisperse structured catalysts is the relative contribution of the macro- and micropore systems to the total variance. In order to gain some insight into this question, it is helpful to define the term

$$\alpha = \frac{(1 - \theta_y)\,\theta_x^2\,(1 + K_a)^2}{[\theta_y + (1 - \theta_y)\,\theta_x\,(1 + K_a)]^2}\left[\frac{R_x}{R_y}\right]^2\left[\frac{D_y}{D_x}\right] \qquad (28)$$

which is the micro-macro ratio of the last two terms of Equation (21). Then the macropore contribution to the variance expressed as a percentage of the total diffusion contribution is $100/(1 + \alpha)$. As an example, consider a typical high surface area alumina catalyst support having the following properties: $\theta_x = 0.5$, $\theta_y = 0.15$, $R_x = 0.0050$ cm (for example, Mischke and Smith, 1962) $R_y = 0.3$ cm, $r_x = 20$ Å, $r_y = 5000$ Å. For argon diffusing in a carrier gas of helium at 1 atm pressure and 25°C, the effective diffusivities in the macropore and micropore structures are estimated to be $D_y = 0.024$ cm²/s and $D_x = 0.00088$ cm²/s, respectively, using methods presented in Satterfield (1970). Upon substitution of these values into Equation (28), the percentage macropore contribution is estimated to be over 99% of the total. (The value chosen for K_a affects this calculation only slightly.) In zeolites the diffusion is often characterized by a strong molecule-wall interaction, and diffusivities may be orders of magnitude smaller than those observed in amorphous catalysts. For example, Barrer and Brook (1954) report diffusivities of argon in sodium mordenite of the order of 10^{-11} cm²/s. A computation for a zeolite catalyst with the following properties: $\theta_x = 0.5$, $\theta_y = 0.15$ $R_x = 0.00005$ cm (for example, Barrer and Brook, 1954; Ruthven and Loughlin, 1971), $R_y = 0.3$ cm, $D_x = 10^{-11}$ cm²/s, $D_y = 0.024$ cm²/s, results in a macropore contribution of only 2%. Thus, while GC effective diffusivity measurements on particles of amorphous catalysts might reflect diffusion in the macropores primarily, measurements on zeolites might reflect contributions from the micropores.

If one compares values of the effective diffusivity of gases in zeolites obtained by the GC-technique with values obtained by other transient response techniques, it is observed that the GC values are higher by several orders of magnitude. For example, Eberly's (1969) GC determinations of the effective diffusivities of argon and krypton in sodium mordenite are nine orders of magnitude higher than corresponding values reported by Barrer and Brook (1954). There appear to be at least two possible explanations for this puzzling observation. The most obvious is that the GC measurements were actually reflecting diffusion in macropores. But in many instances activation energy arguments would tend to discount this possibility. A second possible explanation becomes apparent upon comparison of Equations (23) and (21), representing the old and new calculation procedures respectively. If the macropore diffusivity D_y is very large, then the macropore term in Equation (21) can be neglected and

$$\sigma^2 = \frac{\tau^2}{12} + \frac{2LD_z}{v^3}\left[\theta_z + (1-\theta_z)\,\theta_y + (1-\theta_z)(1-\theta_y)\,\theta_x\right]^2 + \frac{2L(1-\theta_z)\left[\theta_y + (1-\theta_y)\,\theta_x\right]^2 R_y}{3vk_f} + \frac{2L(1-\theta_z)(1-\theta_y)\,\theta_x{}^2 R_x{}^2}{15vD_x} \tag{29}$$

[Here the adsorption term has been neglected. While the correction for adsorption is significant in this example (Eberly, 1969), it is small as compared with the observed discrepancy of nine orders of magnitude.] The total porosity in Equation (23) is the sum of the macropore and micropore porosities. Upon replacing θ with $\theta_y + (1 - \theta_y)\,\theta_x$ Equation (23) is identical with Equation (29) except for the term involving the effective diffusivity. From the equality of σ^2 one obtains the ratio of the effective diffusivities computed from the two models as

$$\frac{D_x}{D} = \frac{(1-\theta_y)\,\theta_x{}^2 R_x{}^2}{\left[\theta_y + (1-\theta_y)\,\theta_x\right]^2 R_y{}^2} \tag{30}$$

For the example cited here this factor is estimated to be 1.5×10^{-8}. In view of the approximate nature of the estimates used for some of the physical properties, in particular R_x, and recognizing that real differences are likely to have been present in the two samples of sodium mordenite, it is believed that the proposed model for a bidisperse structured catalyst satisfactorily explains the unreasonably large values that are often reported in studies employing the GC diffusivity technique.

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NOTATION

A = $2l$ = eddy diffusion term of Equation (27), cm
B = $2\eta D_{AB}$ = molecular diffusion term of Equation (27), cm^2/s
C = quantity defined by Equation (26), s
C = gas phase concentration of diffusing species, gmole/cc
$\tilde{C}$ = transformed concentration variable
C_a = concentration of adsorbed species, gmole/cm^2
D = diffusion or dispersion coefficient based on total area, cm^2/s
D_{AB} = binary diffusion coefficient, cm^2/s
H = plate height, cm
k_f = external film mass transfer coefficient, cm/s
K_a = adsorption Constant, Equation (5)
l = scale of dispersion, cm
L = column length, cm
m_n = nth moment of chromatogram
N = diffusion flux, gmole/cm^2-s
r = pore radius, cm
R = particle radius, cm
s = Laplace transform variable
S_x = surface area in micropores, cm^2/g
t = time, s
v = superficial velocity, cm/s
x = radial distance from center of microparticle, cm
y = radial distance from center of pellet, cm
z = axial distance from column entrance, cm

Greek Letters

α = quantity defined by Equation (28)
η = molecular diffusibility
θ_x = micropore porosity, cc micropores/cc microparticle
θ_y = macropore porosity, cc macropores/cc pellet
θ_z = column porosity, cc bed voids/cc bed
μ = mean of residence time distribution function, s
ρ = catalyst particle density, g/cc
σ^2 = variance of residence time distribution function, s^2
τ = width of tracer input, s

Subscripts

x = microparticle quantity
y = pellet quantity
z = column quantity
0 = quantity at the column entrance
L = quantity at the column exit
Rx = quantity evaluated at surface of microparticle
Ry = quantity evaluated at surface of pellet

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