Equation (9) requires a knowledge of the flow pattern. The flow pattern must in turn be determined in conjunction with a knowledge of the turbulent momentum transport. It is suggested that methods similar to those employed herein be applied to the momentum transfer problem.

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#### NOTATION

 $d_{\scriptscriptstyle N}$ = diameter of primary jet nozzle = turbulent transfer coefficient,

(lb.m/ft. sec.)

 $P_{P}^{f,g}$ = generation functions

= coordinates of the point P

= radial coordinate, (in. where Rnumerical values are given)

 $R^{+}$ = dimensionless radial coordinate,  $R/d_N$ 

 $R_{o}$ = radial coordinate at the plane of the nozzle, in.

S= distance along a streamline

u= velocity vector

= axial velocity, (ft./sec. where numerical values are given)

radial velocity, (ft./sec. where  $u_{R}$ numerical values are given)

 $\mathbf{v}$ = volume

X = mole fraction of helium

= axial coordinate

 $\mathbf{Z}$ = dimensionless axial coordinate,

#### **Greek Letters**

 $\alpha, \beta = \text{constants (see text)}$ 

= influence functions

= density, (lb.m/cu. ft where numerical values are given)

= mass fraction of species, i

= vector operator (gradient)

#### LITERATURE CITED

1. Berry, V. J., D. M. Mason, and B. H. Sage, Ind. Eng. Chem., 45, 1596 (1953).

2. Burgers, J. M., Lecture notes, California Inst. Technol., Pasadena, California (1951); reported in reference 8. 3. Emmons, H. W., J. Aeronaut. Sci.,

18, 490 (1951). 4. Forstall, Walton, and A. H. Shapiro, (1970) J. Appl. Mech., 17, 399-408 (1950); in Trans. Am. Soc. Mech. Engrs., 72

5. Forstall, Walton, Sc.D. thesis, Mass. Inst. Technol., Cambridge, Massachu-

setts (1949).

6. Hanratty, T. J., and D. L. Flint, A.I.Ch.E. Journal, 4, 132 (1958).

Hinze, J. O., "Turbulence," McGraw-Hill, New York (1959).

8. Ibid. p. 304.

9. *Ibid*. p. 390.

10. Lynn, Scott, W. H. Corcoran, and B. H. Sage, A.I.Ch.E. Journal, 3, 11

11. Mickley, H. S., T. K. Sherwood, and C. E. Reed, "Applied Mathematics in Chemical Engineering," 2 ed., pp. 25-28, McGraw-Hill, New York (1957).

12. Rosensweig, R. E., Sc.D. thesis, Mass. Inst. Technol., Cambridge, Massachusetts (1959).

13. Towle, W. L., and T. K. Sherwood, Ind. Eng. Chem., 31, 457 (1939).
14. Townsend, A. A., "The Structure of Turbulent Shear Flow," Cambridge Univ. Press, Cambridge, England (1956).

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# Axial Dispersion in a Packed Bed

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Until recently the transport of mass in the direction of flow by a diffusion mechanism has been neglected in the study of rate processes in packed beds. Beginning in 1953 a number of theoretical studies (1, 2, 3, 4, 5, 6, 7, 8, 9) and experimental investigations (10, 11, 12, 13, 14, 15) were made to determine the nature and magnitude of the axial diffusion mechanism. The perfect mixing cell model, in which each of the interstices of a packed bed acts as a mixing stage, was proposed by Kramers and Alberda (4) and further investigated by others (2, 14). The experimental measurements of McHenry and Wilhelm (14) verified the deductions of the mixing cell model for gasflow systems.

The measurements of axial diffusion in liquid-flow systems made by Geankoplis and his co-workers (13, 15), Carberry and Bretton (11), Ebach and White (12), and others produced diffusion coefficients that were in sharp disagreement with the perfect mixing cell model. Figure 1 summarizes the results of several of these investigations.

Carberry (11) inferred from his measurements that some kind of capacitive effect appeared to exist. Deans and Lapidus (3) suggested that stagnant fluid regions produced the capacitive effect and from order-of-magnitude considerations estimated that this could account for the discrepancy between the gas-flow and the liquid-flow diffusion coefficients. Turner (8, 9) and Aris (1) have investigated a mathematical model for the capacitive effect in terms of distributed pockets of stagnant fluid in a packed bed. Application to existing experimental data was not made however. In the present investigation an analysis somewhat similar to Turner's, although differing considerably in detail, is applied to reported experiments in axial dispersion.

### THE FILM MODEL

A packed bed can be idealized by dividing each of its interstices into two regions. In one region turbulence produces complete mixing. In the other region the fluid is stagnant, and mixing occurs incompletely by molecular diffusion. The continuity equation for a tracer substance in the fluid is

$$D_{L} \frac{\partial^{2} c}{\partial x^{2}} - \frac{U}{\epsilon_{f}} \frac{\partial c}{\partial x} - \frac{\partial c}{\partial t} - \frac{\epsilon - \epsilon_{f}}{\epsilon_{f}} - \frac{\partial q}{\partial t} = 0$$
 (1)

This equation differs from the one used by earlier investigators only in the appearance of a term that accounts for the holdup in the stagnant fluid and in the use of a so-called effective porosity which is the fraction of the packed bed volume occupied by the perfectly mixed regions. In most of the experiments reported it appears that no large-scale, transverse concentration gradients existed, thus the absence of such terms in Equation (1).

In addition an equation to describe mass transport in the stagnant fluid is required. It will be assumed that such transport occurs only by molecular diffusion and only in the direction transverse to the flow. Furthermore it will be assumed that the stagnant fluid forms a thin film of uniform thickness surrounding the particles in the packed

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bed. This makes it possible to treat the stagnant fluid as a flat film. The continuity equation for the tracer in the stagnant film may then be written as

$$D_m \frac{\partial^2 w}{\partial z^2} - \frac{\partial w}{\partial t} = 0 \tag{2}$$

The actual film thickness will vary from point to point in the packed bed, being greater in the neighborhood of points of contact between particles. Thus the film thickness computed from this analysis will be averaged over the packed bed.

The local concentration w of tracer in the film can be related to the concentration q by the equation

$$q = \frac{1}{\Delta_m} \int_0^{\Delta_m} w dz \tag{3}$$

In other words q is just w averaged over the thickness of the film.

In those experiments which were performed at low Reynolds numbers the film was fairly thick, but Equation (2) is still reasonably accurate if the cross-sectional area for diffusion is based on the average of the surface area of the particles and the interfacial area between the film and the perfectly mixed regions. The averaging process was carried out by treating the packed bed as though it were a bundle of parallel tubes having radii a equal to twice the hydraulic radius of the packed bed; that is one obtains

$$a = \frac{D_{p\epsilon}}{3(1-\epsilon)}$$

The interfacial area can be calculated from the film thickness and the tube geometry. The average is then the arithmetic average of this calculated interfacial area and the known particle area.

Several additional assumptions have been made implicitly in the preceding analysis. The effect that the random interconnection of pores might have on the axial diffusion was ignored. This assumption will be relaxed later by making use of the experimental measurements of McHenry and Wilhelm (14). The effect of the higher fluid velocity near the containing wall of a packed bed has been neglected. One effect that this has is to produce velocity profile mixing, as described by G. I. Taylor (16, 17), which increases the apparent axial diffusion. Its other effect is the result of the analytical methods commonly used in axial dif-fusion experiments. The input and output concentrations to and from the packed bed are measured as averages over the cross section of the bed. Since the concentration changes near the wall are out of phase with those in the center of the bed, the averaging process makes it appear that more diffusion has occurred than is actually the case. Both these effects will be at a minimum

for large ratios of bed to particle diameter.

Finally the stagnant film corresponds to the displacement thickness of a boundary layer. By assuming a stagwhere the bar indicates a complex number. By the use of Equation (10) the ratio of the complex exit amplitude to the complex inlet amplitude of the tracer sine wave is obtained and is

$$\frac{\overline{X}_{\bullet}}{\overline{X}_{\bullet}} = \left\{ \frac{(\alpha - 1) \sinh \left(\frac{\alpha N_{Pe}L}{2D_{p}}\right)}{\sinh \left(\frac{\alpha N_{Pe}L}{2D_{p}}\right) + \alpha \cosh \left(\frac{\alpha N_{Pe}L}{2D_{p}}\right)} + 1 \right\}$$
(11)

nant film the film thickness will be calculated as a smaller quantity than would be the case if the fluid velocity had been accounted for by some method analogous to Kroujiline's energy integral. The ratio of these two thicknesses is a constant, as is shown in boundary-layer theory. The magnitude of this constant is not important as it will be absorbed by other empirical constants that will arise in this analysis.

#### **BOUNDARY CONDITIONS**

Suitable boundary conditions for Equations (1) and (2) depend on the type of experiment being analyzed. There are three basic types: sinusoidal variation, step variation, and pulse variation of the tracer concentration. Only the first type will be discussed here.

The boundary conditions used are based on the discussion by Wehner and Wilhelm (18) and are

$$c_{i} = c_{M} + X_{i} \cos \omega t \quad \text{at } x = 0 - (4)$$

$$c = c_{i} \quad \text{at } x = 0 + (5)$$

$$Uc - \epsilon_{f} D_{L} \frac{\partial c}{\partial x} = Uc_{o} + L_{e} \frac{\partial c_{e}}{\partial t}$$

$$\text{at } x = L -$$

but  $c = c_{\circ}$  at x = L - (6) Thus

$$\frac{\partial c}{\partial x} = \frac{L_{\bullet}}{\epsilon_{f} D_{h}} \frac{\partial c}{\partial t}$$
 (7a)
ose experiments reported the

For those experiments reported the right-hand side of Equation (7a) is very nearly zero; thus it may be written with adequate accuracy as

$$\frac{\partial c}{\partial x} = 0 \qquad \text{at } x = L - (7b)$$

For Equation (2) the boundary conditions are

$$w = c$$
 at  $z = \Delta_m$  (8)  
 $\frac{\partial w}{\partial z} = 0$  at  $z = 0$  (9)

The concentrations  $c_i$  and  $c_e$  are those measured in the analytical cells just preceding and just following the packed bed.

## THE SOLUTION OF THE FILM THEORY EQUATIONS

The system of equations is solved by the well-known method (19) of assuming a solution of the form

$$\overline{c} = \overline{c}_{M} + \overline{X} \exp(i \omega t) \qquad (10)$$

where 
$$\alpha = \sqrt{\frac{(1-\alpha) N_{Pe}L}{2D_{p}}}$$

$$\alpha = \sqrt{\frac{1+\frac{i4\beta}{N_{Pe}^{2}}}{1+\frac{i4\beta}{N_{Pe}^{2}}}}$$

$$\beta = N_{Pe} N_{\Omega} \left\{ 1 - N_{\Delta} \frac{\tanh[\eta(1+i)]}{\eta(1+i)} \right\}$$

$$N_{Pe} = \frac{UD_{p}}{\epsilon_{l}D_{L}}$$

$$N_{\Omega} = \frac{\omega \epsilon D_{p}}{U} (1-\Delta_{m}')^{2}$$

$$N_{\Delta} = \frac{2-\Delta_{m}'}{(1-\Delta_{m}')^{2}} \Delta_{m}'$$

$$\Delta'_{m} = \Delta_{m}/2a$$

$$\eta = \Delta_{m} \sqrt{\frac{\omega}{2D_{m}}}$$

By taking the absolute value of the amplitude ratio (the experimentally measured quantity) and making several approximations (one of which is that  $\eta \leq 0.3$ ) which are well within the experimental error, there results

$$(\Delta'_m)^3 \left(1 - 1/2 \Delta'_m\right) =$$

$$13.5 \frac{D_m \left(1 - \epsilon\right)^2}{D_p U \epsilon}$$

$$\cdot \left(\frac{BU^2}{\epsilon^2 \omega^2 D_p L} - \frac{1}{N_{P\epsilon}}\right) \quad (12)$$

If the film is neglected in Equation (12) it reduces to\*

$$N'_{Pe} = \frac{\epsilon^2 \omega^2 D_p L}{BU^2} \tag{13}$$

which is a close approximation to the equation used by previous investigators to interpret their axial dispersion data. For those few cases where the approximations produced too large an error a more accurate form of the equation was used (20). By means of Equation (13) Equation (12) may be transformed to

$$\frac{1}{N'_{Pe}} - \frac{1}{N_{Pe}} = \frac{1}{13.5} \frac{N'_{Re} N_{Se}}{(1 - \epsilon)^2} (\Delta'_m)^3 (1 - 1/2 \Delta'_m)$$
(14)

This form is convenient in later discussions.

\*The prime on the Peclet number is used to emphasize that the film has been neglected.

The phase angle  $\phi$  of the exit concentration wave with respect to the input wave is also of interest. It is given by

Strang and Geankoplis (15), and Liles (15)

$$\phi = \frac{\omega \epsilon L}{U} \frac{1}{\sqrt{1 + \frac{2}{N_{Pe}} \left(\frac{\omega \epsilon D_p}{U}\right)^2 \left(\frac{1}{N'_{Pe}} - \frac{1}{N_{Pe}}\right)}}$$
(15)

#### CALCULATION OF THE PECLET NUMBER

The problem of estimating the Peclet number appearing in Equations (11), (12), (14), and (15) must now be investigated. Kramers and Alberda (4), Aris and Amundson (2), and others have discussed the mixing cell model of axial dispersion for the case of no film. They found that for perfect mixing cells the Peclet number should be a constant having value of  $2/\gamma$ , where  $\gamma$ is inversely equal to the number of interstices per particle diameter.

A simple extension of their analyses shows that even in the presence of a film the Peclet number will have the same value except that it is necessary to replace  $\bullet$  of the packed bed by  $\epsilon_t$ which, it will be recalled, is the volume fraction of the bed occupied by the perfectly mixed fluid.

For packed beds consisting of wellordered arrays of particles  $\gamma$  is easily calculated from the geometry of the array. Unfortunately in all the experiments reported random arrays of particles were used. y can still be approximated from experiments in which film effects are absent. Order-of-magnitude calculations indicate that the film effects are negligible in the gas-flow experiments of McHenry and Wilhelm (14) because of the high molecular diffusivity of gases. The use of an experimental value for the Peclet number has the further advantage that if there is an appreciable mixing effect resulting from the random interconnection of the interstices, it will be included. Therefore the McHenry and Wilhelm value of 1.88 will be used for the Peclet number.

#### COMPARISON OF THEORY WITH PUBLISHED DATA

Four groups of investigators (12, 13, 14, 15) have reported large amounts of

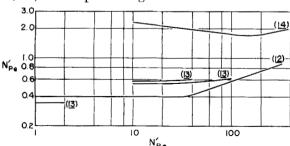


Fig. 1. The apparent Peclet number vs. Reynolds number as reported by several investigators.

and Geankoplis (13) were with liquids. McHenry and Wilhelm (14) experimented with gases. In all these reports it was assumed that no film exists, so that the data could be interpreted by a diffusion equation

data obtained by the frequency re-

sponse technique. Of these the experi-

ments of Ebach and White (12),

$$D_{L} \frac{\partial^{2} c}{\partial x^{2}} - \frac{U}{\epsilon} \frac{\partial c}{\partial x} - \frac{\partial c}{\partial t} = 0 \quad (16)$$

By means of Equation (16) and the experimental data the diffusivity  $D_L$ was calculated and reported in terms of an apparent Peclet number  $(N'_{Pc} \equiv$  $UD_p/\epsilon D_L$ ) vs. a modified Reynolds number  $(N'_{R_0} \equiv UD_p/\nu)$ . Figure 1 shows these results. The sharp disagreement between the liquid and the gas results is to be noted.

Figure 2 shows the liquid data interpreted by Equation (12), the film model, and plotted as  $(\Delta_m/D_p)$   $(N_{Se}/1000)^{0.42}$  vs. the Ergun (21) form of the Reynolds number. Film thicknesses for the gas data have not been calculated because the gas data are insensitive to the film thickness. From the figure it can be seen that the mixing film theory correlates the axial dispersion data well.

The experiments that have been performed included special experiments to test the applicability of a Fick's law equation [Equation (16)] to the axial dispersion. The experiments of Mc-Henry and Wilhelm may be disregarded because the film effect was ab-

Liles and Geankoplis varied the frequency of their sine wave input and also the length of the packed bed while holding the fluid velocity constant. They found that the apparent Peclet number was unaffected and concluded that this meant that Equation (16) was valid and that bed capacitance effects (for example film effects) were absent. Equation (12) indicates that even in the presence of a film, variations of the frequency and bed length will have no effect on the apparent Peclet number. This results from the fact that the quantity B is still related to frequency and bed length in the same way as for the no-

They also calculated (by  $\phi =$  $\omega \in L/U$ ) and measured phase angles for a bed 67.3 cm. long containing spherical particles 6.13 mm. in diameter. By varying  $\omega \epsilon/U$  they could vary the phase angle. At high phase angles their calculations slightly overestimated the phase angle. This small discrepancy is explained by the film theory [see Equation (15)].

#### THE MIXING FILM AND THE MASS TRANSFER FILM

The mixing film theory of axial mixing correlates the axial dispersion data adequately; since it is an ad hoc concept, a comparison with films calculated from other processes such as mass transfer is desirable to show whether the concept has a physical basis. Most of the published mass transfer data have been critically reviewed by Ergun (22). He finds that the best liquidsystem mass transfer data for randomly packed beds appear to be those of McCune and Wilhelm (23) and Gaffney and Drew (24). Accordingly these data will be used to calculate the mass transfer film thickness. In the following this will be called the diffusion film.

For a packed bed in which steady state mass transfer is occurring the mass conservation equation for the flowing fluid is

$$-D_{L}\frac{\partial^{2}c}{\partial x^{2}} + \frac{U}{\epsilon_{f}}\frac{\partial c}{\partial x} = \frac{6(1-\epsilon)}{D_{p}\epsilon_{f}}D_{m}\left(\frac{\partial c}{\partial r}\right)_{w}$$
(17)

The subscript w refers to the magnitude of the quantity at the solid surface. For the stagnant fluid the usual

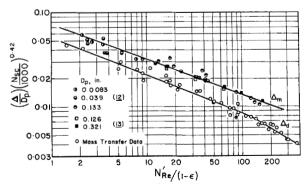


Fig. 2. The correlations of mixing film and mass transfer film thicknesses.

diffusion equation applies, and it is convenient to express it in cylindrical coordinates as

$$\frac{D_m}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c}{\partial r} \right) = 0 \qquad (18)$$

The above equations differ from the usual mass transfer theory only in minor ways: in keeping with the spirit of this report an axial diffusion term has been introduced, and the mass transfer has been expressed in terms of the molecular diffusivity and a stagnant film rather than in terms of the mass transfer coefficient. Again it has been assumed that the interstices may be idealized as a set of parallel tubes of radius a. Arbitrary radial positions are represented by r.

are represented by r.

Equation (18) integrates immediately to

$$r \frac{\partial c}{\partial r} = C \tag{19}$$

Evaluating this expression at r = a one gets

$$\left(\frac{\partial c}{\partial r}\right)_{w} = C/a \tag{20}$$

C may be evaluated by integrating Equation (19) over the thickness of the diffusion film  $\Delta_d$ . After substitution into Equation (20) the result is

$$\left(\frac{\partial c}{\partial r}\right)_{w} = \frac{c - c^{*}}{a \ln\left(1 - \frac{\Delta_{d}}{a}\right)} \quad (21)$$

where  $c^*$  is the concentration at the fluid-solid interface. Equation (21) may be substituted into Equation (17) which then becomes an ordinary differential equation; thus

$$-D_{L}\frac{d^{2}c}{dx^{2}} + \frac{U}{\epsilon_{f}}\frac{dc}{dx} - \frac{2\epsilon}{\epsilon_{f}}\frac{D_{m}(c - c^{\bullet})}{a^{2}\ln(1 - \Delta_{d}/a)} = 0 \quad (22)$$

The boundary conditions are

$$c = c_i \qquad \text{at } x = 0 \tag{23}$$

$$dc/dx = 0 \quad \text{at } x = L$$

$$c = c_{\theta} \quad \text{at } x = L$$

$$(24)$$

The solution of these equations for a bed of length L is

$$\frac{c_{e} - c^{\bullet}}{c_{i} - c^{\bullet}} = \frac{2\lambda \{\exp[-N_{Pe}(\lambda - 1) L/2D_{p}]\}}{\lambda (1 - e^{-N_{Pe}\lambda L/D_{p}}) + (1 + e^{-N_{Pe}\lambda L/D_{p}})}$$
(25)

where

here
$$\lambda = \sqrt{1 - \frac{24 (1 - \epsilon) D_m}{N_{Pe} Ua \ln (1 - \Delta_d/a)}}$$

For the experimental data obtained by Gaffney and Drew (24) and Mc-Cune and Wilhelm (23) the coefficient of the term in braces in Equation (25) ranges from 1.0007 to 1.05. Thus no serious error is introduced if the coefficient is set equal to unity. Equation (25) then reduces to

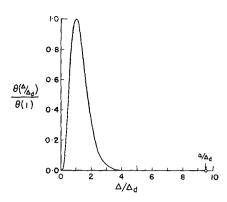


Fig. 3. The film thickness distribution at a Reynolds number of 10.

$$\ln \frac{c_{i} - c^{*}}{c_{e} - c^{*}} = \frac{N_{Pe}L}{2D_{P}} (\lambda - 1)$$
(26)

or, in a more convenient form

$$-\ln\left(1 - \Delta_d/a\right) = \frac{6\left(1 - \epsilon\right)D_mL}{UaHD_p\left(1 + \frac{HD_p}{N_{P}L}\right)}$$
(27)

where

$$H = \ln \frac{c_i - c^*}{c_e - c^*}$$

By means of Equation (27) the diffusional film thickness  $\Delta_d$  may be calculated from mass transfer data.

The axial dispersion term  $1 + HD_p/N_{Pe}L$  ranged from 1.001 to 1.047; therefore axial dispersion had almost no effect on mass transfer in the liquid systems. This confirmed Ergun's (22) observation that axial dispersion effects appeared to be absent in liquid system mass transfer experiments.

For thin films (that is  $\Delta'_d \ll 1$ ) Equation (27) may be approximated by

$$\Delta'_{d} = \frac{6 \left(1 - \epsilon\right) D_{m}L}{UaHD_{p} \left(1 + \frac{HD_{p}}{N_{Pe}L}\right)}$$
(28)

which shows that H is approximately inversely proportional to  $\Delta'_d$ . The approximation holds within 5% for values of  $\Delta'_d < 0.10$ . This includes nearly all the mass transfer data used.

With the data mentioned (23, 24) and Equation (27) film thicknesses were calculated and plotted as  $(\Delta_d/D_p)$   $(N_{sc}/1000)^{0.42}$  vs.  $N'_{Ed}/(1-\epsilon)$  in Figure 2. The Schmidt number dependence is usually given to the 1/3 power rather than the 0.42 power. However Caffney and Drew (24) showed that 0.42 power yields a better correlation. Furthermore experiments by Bedingfield and Drew (25) on mass and heat transfer from single cylinders indicated that 0.44 gave a better correlation than did 1/3. The two reports above appear

to be the only experimental works that have carefully investigated the proper exponent for the Schmidt number.

It will be noted that the diffusion film is substantially thinner than the mixing film. This occurs because in each case an average film thickness has been calculated. It is evident, as Hoelscher (26) has pointed out, that in a packed bed there must be a distribution of film thicknesses rather than a constant film thickness.

For the diffusion film the magnitude

of 
$$H\left(H=\ln rac{c^{ullet}-c_{\scriptscriptstyle 1}}{c^{ullet}-c_{\scriptscriptstyle 2}}
ight)$$
 is inversely

proportional to the film thickness. Therefore the average diffusion film thickness  $\Delta_d$  is related to the local values  $\Delta$  by

$$\Delta_d = (\overline{\Delta^{-1}})^{-1} \tag{29}$$

On the other hand for the mixing film [see Equation (12)] the thickness  $\Delta_m$  is related to the local values by

$$\Delta_m = (\overline{\Delta^3})^{1/3} \tag{30}$$

From this it is evident that for a distributed film  $\Delta_m > \Delta_a$ ; in addition the broader the distribution function, the greater will be the difference between  $\Delta_m$  and  $\Delta_a$ .

The question that still remains however is whether the difference between  $\Delta_d$  and  $\Delta_m$  can be accounted for by the distribution of film thicknesses. This question cannot as yet be answered rigorously because no independent data exist on film distributions. Thus it is necessary to choose some reasonable distribution function on the basis of limited information. Hoelscher (26) has suggested that the beta distribution of the first kind, well known in statistics (27), has suitable properties.

Calculations for the current problem with the beta distribution are unwieldy. Another function which has almost all of the desirable properties of the beta distribution is a modification of the gamma distribution (27). The only disadvantage of the gamma distribution is that it has no upper limit; that is it allows infinite film thicknesses. Fortunately in the present case it represents a sharply peaked function, so that the fraction of the film having large film thicknesses is negligible.

The modified gamma function for the film thickness is

$$\theta(\Delta/\Delta_d)d(\Delta/\Delta_d) = h(\Delta/\Delta_d)^k e^{-m\Delta/\Delta_d} d(\Delta/\Delta_d) \quad (31)$$

Expression of the film thickness as the dimensionless number  $\Delta/\Delta_a$  puts no restriction on the function but is done because it turns out to be convenient. The fraction of the film having thicknesses lying between  $\Delta$  and  $\Delta + d\Delta$  is  $\theta(\Delta/\Delta_a)d(\Delta/\Delta_a)$ . The constants h, k,

and m will be fixed by the requirement that the probability of finding  $\Delta$  between zero and infinity is unity, the necessity of fitting  $(\overline{\Delta^{-1}})^{-1}$  to  $\Delta_d$ , and fitting  $(\overline{\Delta^3})^{1/3}$  to  $\Delta_m$ . The result is

$$\theta(\Delta/\Delta_d)d(\Delta/\Delta_d) =$$

$$\frac{1}{\Gamma(m)} \left( m \frac{\Delta}{\Delta_d} e^{-\Delta/\Delta_d} \right)^m d(\Delta/\Delta_d)$$
(32)

where m may be found from

$$\frac{\Delta_m}{\Delta_d} = \left[ \frac{(m+3)(m+2)(m+1)}{m^3} \right]^{1/3}$$
(33)

From the experimental results (Figure 2) a typical value of m may be calculated to see if it yields a reasonable film distribution. At a Reynolds number of 10 the ratio  $\Delta_m/\Delta_d$  is 1.537, for which m = 3.62. In Figure 3 the resulting distribution is plotted as  $\theta(\Delta)$  $\Delta_d$ )/ $\theta$ (1) vs.  $\Delta/\Delta_d$ . Note that the ratio of the radius of the interstices a to the average diffusion film thickness  $\Delta_d$ (that is  $a/\Delta_a = 9.52$  for  $N_{sc} = 1,000$ ) is also plotted.

From Figure 3 it can be seen that the resulting distribution curve looks quite reasonable. It is sharply peaked, and the probability of finding a film thickness greater than the pore radius is negligibly small. This does not prove that  $\Delta_m$  and  $\Delta_d$  are simply two different manifestations of the same distributed film, but it does make such a belief reasonable.

#### CONCLUSIONS

It has been shown that the discrepancy between the axial Peclet numbers for gas-flow and liquid-flow experiments can be explained by including the effect of a stagnant film. This film has been compared with the stagnant film calculated from mass transfer experiments. If the distribution of film thicknesses in a packed bed is taken into account, it appears that the two kinds of films are the same.

If one refers again to the basic differential Equations (1) and (2), it may be seen that the mixing film will have an effect on dispersion only in unsteady state processes. In steady state processes, such as a typical catalytic reactor, the Peclet number will be approximately 2, whether for gas- or liquid-flow systems.

In typical unsteady state processes, for example adsorbers and regeneration pebble bed heaters, diffusion of heat or mass within the particles will be substantially more significant than diffusion through the film; here too it may be possible to simply use a Peclet number of about 2.

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#### NOTATION

B

 $=\frac{D_{p\epsilon}}{3(1-\epsilon)}$ , pore radius, L

 $\boldsymbol{C}$ = integration constant,  $ML^{-3}$ 

= tracer concentration,  $ML^{-3}$ 

= concentration in exit analytical cell.  $ML^{-3}$ 

= concentration in entrance ana-Cı lytical cell, ML-

= time averaged tracer concentration,  $ML^{-3}$ 

= equilibrium concentration,  $\hat{ML}^{-3}$ 

 $\left(\frac{\partial c}{\partial r}\right)_w$  = value of the derivative at

the fluid-solid interface,  $ML^{-4}$ ⇒ axial dispersion coefficient,  $D_{\scriptscriptstyle L}$ 

= molecular diffusivity of tracer in solution,  $L^2T^{-1}$ 

 $D_p$ = particle diameter, L

Н = see Equation (27) = constant

constant

= length of packed bed, L

= length of analytical cell, L

= constant

= Peclet number  $N_{Pe}$ 

= see Equation (13), apparent

Peclet number

 $N'_{Re} = \frac{\overline{D_p U}}{\nu}$ , modified Reynolds num-

 $=\frac{\nu}{D_{m}}$ , the Schmidt number

= see Equation (11) = see Equation (11)

= average tracer concentration

in the stagnant film, ML-3

radial distance, L

= time, T

= superficial velocity,  $LT^{-1}$ 

= local tracer concentration in film,  $ML^{-3}$ 

X = complex concentration amplitude,  $ML^{-3}$ 

 $\overline{X_e}$ = complex concentration amplitude in exit analytical cell,

= concentration amplitude in in- $X_{i}$ let analytical cell,  $ML^{-3}$ 

= distance measured from enxtrance of packed bed, L

distance measured from pore wall, L

#### **Greek Letters**

= see Equation (11)

= see Equation (11)

= number of particle lengths per mixing cell

Δ = local film thickness, L

= diffusion film thickness, L  $\Delta_d$ 

 $\Delta'_{d}$  $= \Delta_d/a$ 

 $\Delta_m$ = mixing film thickness, L

 $= \Delta_m/a$ = porosity of packed bed

= apparent porosity of packed

= see Equation (11)

 $\theta(\Delta/\Delta)_a$  = generalized gamma distribution

= see Equation (25)

= kinematic viscosity,  $L^2T^{-1}$ 

= phase angle

= radian frequency of concentration wave, T-1

#### LITERATURE CITED

- 1. Aris, Rutherford, Chem. Eng. Sci., 10,
- 80 (1959).

  A.I.Ch.E. Journal, 3, 280 (1957).

  TI A and Leon Lapidus, ibid.,
- 6,656 (1960).
- Kramers, H., and G. Alberda, Chem. Eng. Sci., 2, 173 (1953).
   Saffman, P. G., J. Fluid Mech., 6,
- (1959). Chem. Eng. Sci., 11, 125
- 7. ——, J. Fluid Mech., 7, 194 (1960). 8. Turner, G. A., Chem. Eng. Sci., 7, 156
- (1957).
- 9. Ibid., 10, 14 (1959).
- 10. Cairns, E. J., and J. M. Prausnitz, ibid., 12, 20 (1960).
- Carberry, J. J., and R. H. Bretton, A.I.Ch.E. Journal, 4, 367 (1958).
   Ebach, E. A., and R. R. White, ibid.,
- p. 161.
- Liles, A. W., and C. J. Geankoplis, *ibid.*, **6**, 591 (1960).
- 14. McHenry, K. W., Jr., and R. H. Wilhelm, *ibid.*, 3, 83 (1957).
- 15. Strang, D. A., and C. J. Geankoplis, Ind. Eng. Chem., 50, 1305 (1958). Taylor, G. I., Proc. Roy. Soc., 219A,
- 186 (1953).

- 186 (1953).
   17. Ibid., 223A, 446 (1954).
   18. Wehner, J. F., and R. H. Wilhelm, Chem. Eng. Sci., 6, 89 (1956).
   19. Wylie, C. R., Jr., "Advanced Engineering Mathematics," p. 93, McGraw-Hill, New York (1951).
- Gottschlich, C. F., Ph.D. dissertation, Univ. Cincinnati, Cincinnati, Ohio (1961).
- 21. Ergun, Sabri, Chem. Eng. Progr., 48, 89 (1952)
- 22. Ibid., 227 (1952).
- McCune, L. K., and R. H. Wilhelm, Ind. Eng. Chem., 41, 1124 (1949).
   Gaffney, B. J., and T. B. Drew, ibid.,
- p. 112Ó.
- Bedingfield, H. H., Jr., and T. B. Drew, *ibid.*, 42, 1164 (1950).
   Hoelscher, H. E., A.I.Ch.E. Journal, 4,
- 300 (1958).
- Weatherburn, C. E., "A First Course in Mathematical Statistics," Cambridge Univ., England (1946).

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