A Boundary-Layer Model of Fluid-Particle Mass Transfer in Fixed Beds

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The process of fluid-particle mass transfer in fixed beds at Reynolds numbers less than 1,000 is viewed in terms of transient molecular diffusion within a boundary layer which is developed and destroyed repeatedly as the fluid journeys through the bed. Literature data support the *j* factor derived from the premises of the model. The theory predicts a Schmidt number exponent of 2/3 for $N_{Sc} \geqq 1$; however this exponent should approach 1/2 for $N_{Sc} < 1$.

While numerous empirical correlations exist which permit the determination of mass transfer coefficients for fluid-particle exchange in fixed beds (*10, 11, 15, 22, 30*), it is nevertheless of some interest to explore these events from a theoretical point of view. To date the most interesting rationalization of fixed bed mass transfer is found in the recent work of Thoenes and Kramers (*28*) who interpreted their data in terms of mass transfer from a particle into a fluid network composed of laminar, turbulent, and stagnant regimes. The present work attempts to establish a rationale in terms of a simplified boundary-layer theory. Although this study is confined to mass transfer, the model may well be extended to heat transfer in fixed beds.

Higbie (*14*) made one of the earliest attempts to relate the average mass transfer coefficient to the species diffusivity and the average time of fluid element exposure to sink or source by

$$\bar{k} = 2\sqrt{\frac{D}{\pi\theta}} \qquad (1)$$

Higbies' theory has been verified in investigations in which the boundary conditions inherent in the model have been satisfied experimentally (*7, 21, 26*). One of the key and limiting assumptions in this model is that specifying the absence of a velocity gradient at the transfer interface. Transfer processes between a solid and flowing fluid obviously occur across a boundary at which a velocity gradient must exist; consequently the influence of velocity upon the diffusive process must be assessed. In the case of simple geometries the transfer processes may be readily predicted for an assumed velocity distribution. Heat transfer literature reveals well-known examples such as the solution of Leveque (*18*) for heat transfer between a laminar fluid and a pipe wall. Kramers (*17*) applied an analogous model to mass transfer from a wall to a laminar falling film.

In the instance of turbulent exchange Hanratty (*13*) has made a significant contribution by applying the Higbie-Danckwerts penetration model to predict the experimental concentration-profile data found in the mass transfer studies of Lin, Moulton, and Putnam (*19*). Since the data treated were obtained in the region of turbulent flow, it is apparent that the exchange involved transfer from the source to eddies, and therefore the velocity gradient in the fluid has no influence upon the diffusive process. In a comparable circumstance Johnson and Huang (*16*) found evidence to support the penetration model in their study of solids dissolution in an agitated vessel. It should be emphasized that an independent evaluation of θ is not possible in exchange events between eddies and a sink or source, and evidence for support of Higbie theory or the Danckwerts modification thereof rests upon finding a ½ power dependence of the transfer rate upon the Schmidt number.

DIFFUSION WITHIN A DEVELOPING BOUNDARY LAYER

Higbie's model follows via solution of

$$\frac{\partial c}{\partial \theta} = u\frac{\partial c}{\partial x} = D\frac{\partial^2 c}{\partial y^2} \qquad (2)$$

where the fluid velocity is invarient in x and y. It will prove fruitful however to express u as a function of these distance variables as

$$u/u_a = (Ky)^a/\left(\frac{\nu x}{u_a}\right)^b \qquad (3)$$

Thus Equation (3) becomes

$$u_a\frac{\partial c}{\partial x} = \left(\frac{\nu x}{u_a}\right)^b \frac{D}{(Ky)^a}\frac{\partial^2 c}{\partial y^2} \qquad (4)$$

Mixon and Carberry (*24*) have obtained a solution to Equation (4), expressing the average mass transfer coefficient in terms of the exponents a and b:

$$\bar{k} = \left[\frac{(a+2)}{(a+2)-(b+1)}\right] \frac{[(b+1)K]^{1/(a+2)}(a+2)^{a/(a+2)}D^{(a+1)/(a+2)}}{\Gamma[1/(a+2)](x/u_a)^{(b+1)/(a+2)}\nu^{b/(a+2)}} \qquad (5)$$

It will be recognized that the fluid velocity component in the y direction, perpendicular to flow, has been ignored in formulating the basic differential equation. The author has assumed that the term $v\,\partial c/\partial y$ is negligible relative to $u\,\partial c/\partial y$. A consideration of the perpendicular component alters the coefficient of the derived relationship [Equation (14)] by about 20%, but in no way is the indicated functionality changed (*24*).

Equation (5) reduces readily to a number of interesting cases corresponding to various value of a and b:

$a = b = o$, Higbie's model.

$$\bar{k} = 2\sqrt{\frac{D}{\pi\theta}} \text{ where } \theta = X/u_a \qquad (6)$$

$a = 1$, $b = o$, Leveque approximation

$$\bar{k} = 0.808\left(\frac{KD^2}{x/u_a}\right)^{1/3} \qquad (7)$$

Equation (7) is identical to that derived by Kramers (*17*) for solid dissolution into a falling film.

The instance of diffusion within a developing boundary layer is approximated by $a = 1$ and $b = ½$; that is

$$u/u_a = Ky/\sqrt{\frac{\nu x}{u_a}} \qquad (8)$$

Boundary-layer theory (*27*) teaches that the linear velocity approximation is

$$u/u_\infty = y/\sqrt{\frac{12\nu x}{u_\infty}} \qquad (9)$$

If the velocity at the boundary-layer edge, u_∞, is expressed in terms of the average as $u_\infty = 2u_a$, Equation (9) reduces to

$$u/u_a = 0.815\,y/\sqrt{\frac{\nu x}{u_a}}, \quad \therefore K = 0.815 \qquad (10)$$

For $a = 1$ and $b = ½$ Equation (5) becomes

$$\bar{k} = \frac{1.15\,D^{2/3}}{(x/u_a)^{1/2}\nu^{1/6}} \qquad (11)$$

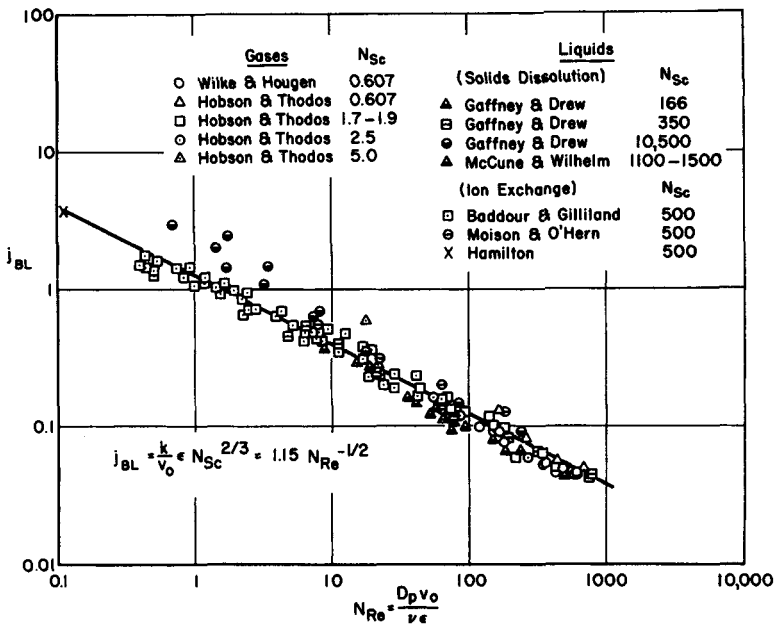

Fig. 1. Fixed bed mass transfer in terms of boundary-layer theory.

APPLICATION TO FIXED BED TRANSFER PROCESSES

The precise characterization of flowing fluid behavior in a fixed bed is hardly possible at this time. It is perhaps equally difficult to define the geometry of the fixed phase as it is seen by the flowing fluid. Nevertheless if the fixed bed is viewed as a series of discrete surfaces separated at points by void cells, it might be argued that in the flow regime below fully developed turbulence the fluid, in its journey through the bed, must experience a succession of boundary-layer developments and destructions. During a given boundary-layer development over a distance x diffusion or penetration of a species will occur between fluid and the fixed surface. If it is assumed that the velocity within the developing boundary layer at the transfer boundary can be approximated by Equation (10), then the specification of $\overline{k}$ by Equation (11) is possible if x can be defined for a fixed bed.

A specification of x is possible in the light of recently acquired axial-dispersion data for fixed beds which suggest that, for gases, mixing of a perfect nature occurs about once every particle diameter (23). Liquid-dispersion data present a more complex problem (4, 6); however if a model suggesting imperfect fluid mixing in each void cell is tolerable (5), then in terms of the developing boundary-layer notion it can be argued that the boundary layer ought to suffer destruction at the mixing points. In other words the boundary layer develops and collapses over a distance approximately equal to one particle diameter.

Thus letting

$$x = D_p = \frac{\nu N_{Re}}{u_a} \qquad (12)$$

and recalling the definition of the Schmidt number, $N_{Sc} = \nu/D$, one can reduce Equation (11) to

$$\overline{k} = 1.15\, u_a\, N_{Re}^{-1/2}\, N_{Sc}^{-2/3} \qquad (13)$$

In terms of a boundary layer j factor, bed void fraction, and the average superficial velocity based upon tube cross-sectional area

$$j_{BL} = \frac{\overline{k}}{u_o}\,\epsilon\, N_{Sc}^{2/3} = 1.15\, N_{Re}^{-1/2} \qquad (14)$$

A comparison of the theoretical relation with empirical correlations indicates that the literature j factors are usually based upon superficial velocity. Thus the derived equation can be tested against experimental data by correcting the published j factors with the void fraction encountered in the experiments and plotting the resulting j values against the Reynolds number based upon average velocity in the bed. Figure 1 displays the comparison of literature data with Equation (14). A Schmidt number variation of from 0.6 to 10,500 is represented by the data for such diverse transfer processes as vaporization, solids dissolution, dilute solution ion exchange, and chromatography. The agreement between data and theory is quite good with the exception of the low Reynolds number data of Gaffney and Drew for $N_{Sc} =$ 10,500. These authors noted however that natural-convection effects were evident in that system at low flow rates. The data of Baddour and Gilliland (1) for dilute solution ion exchange are shown in the j factor form as recalculated and presented by Moison and O'Hern (25).

Obviously not all of the literature data were considered in testing the theory. Ergun (9) has made a critical examination of fixed-bed mass transfer data, and the literature utilized in the present instance was chosen from those studies which evidenced reproducibility and absence of axial mixing effects as noted by Ergun. The latter problem was found to be a prominent one (9) and has been discussed previously (3, 8, 20).

DISCUSSION

The limits of applicability of the derived equation deserve comment. In view of the model invoked Equation (14) should be applicable until the flow rate approaches the value corresponding to turbulent boundary-layer development. The precise value of the Reynolds number at which the transition occurs in a packed bed is difficult to specify. If the character of the packed-bed friction factor-Reynolds number functionality as well as axial dispersion-flow rate relationships (4) permit an inference, then fully developed turbulent flow and therefore turbulent boundary-layer development takes place in the Reynolds number region of about several hundred. The data shown in Figure 1 would suggest that the model is valid to about N_{Re} of 1,000.

The lower flow regime limit of applicability is difficult to define in view of the natural-convection effects on one hand and the specification of x on the other. It is not inconceivable that at very low rates of flow, boundary-layer development may occur over a distance greater than one particle diameter. Thus x itself becomes a function of flow rate; that is $x \propto 1/N_{Re}$ at $N_{Re} << 1$. Such a circumstance would lead to a decrease in j with decreasing values of N_{Re}, a result verified recently by the data of Bar-Ilan and Resnick (2) and more recently by Hamilton (12).

TRANSFER RATES AT THE WALL

The recent work of Yagi (32) on heat and mass transfer at the wall of the packed bed might be interpreted in the light of the boundary-layer notion developed here. Data for mass transfer between water and the coated-tube wall of a packed bed were correlated by Yagi with the equation

$$j_D = \frac{\bar{k}}{u_o}(N_{Sc})^{2/3} = 0.60\,N_{Re'}^{-1/2};\ N_{Re'} < 40 \qquad (15)$$

When one assumes an average void fraction of 0.4, the above relationship may be written on the basis of the average fluid velocity within the bed:

$$j_D = \frac{\bar{k}}{u_o}\epsilon\,N_{Sc}^{2/3} = 0.38\,N_{Re}^{-1/2};\ N_{Re} < 100 \qquad (16)$$

While this functionality is identical to that derived above [Equation (14)], the j relations differ by a constant factor of about 3. In terms of the model suggested in this work the wall transfer data would tempt one to speculate that the boundary layer at low flow rates along the wall of a packed bed develops over a distance equivalent to several particle diameters. Thus Equation (14) is perhaps best written for both transfer at the tube wall and fluid-particle transfer at low values of N_{Re} as

$$j_{BL} = 1.15\,(nN_{Re})^{-1/2} \qquad (17)$$

An alternative model of wall-fluid heat transfer has been presented by Hanratty (*13a*).

The anomalies at low Reynolds numbers and the transfer events at the wall of a packed bed present opportunities for further experimentation designed in a manner which will confirm or deny mechanistic speculations. A quantitative specification of n and its dependence upon velocity near the wall is required to clarify the rate process at that point, while the relationship between n and the Reynolds number must be determined to rationalize particle-fluid exchange data at very low flow rates. Studies of wall-fluid transfer rates in which the inner surface of the packed tube is corrugated or coated with pellets identical to the packing should reveal the extent to which presence of a smooth exchange surface extends the boundary-layer life and thereby reduces the average exchange rate at the wall.

SCHMIDT NUMBER FUNCTIONALITY

Equation (5) states that the exponent upon the Schmidt number is governed by the value of the term $(a+1)/(a+2)$. Hence the exponent must always lie between 1/2 and 2/3 as the velocity at the transfer boundary is either a linear or less than linear function of distance ($1 \geqq a \geqq 0$). The reasoning which follows may clarify this point.

Where the diffusivity of the species is low (high Schmidt number), the region of transfer resistance most certainly lies within the hydrodynamic boundary layer. However systems characterized by high diffusivity, $N_{Sc} < 1$, present an interesting circumstance in which the concentration boundary layer becomes larger than the hydrodynamic one. In other words the hydrodynamic boundary layer tends, by reason of rapid diffusion, to become saturated in the case of transfer from the surface to the fluid. Under these circumstances the transfer rate will no longer be governed by the velocity gradient at the surface but dictated by the velocity gradient at a point closer to the hydrodynamic boundary-layer edge. To the extent that the velocity profile is nonlinear at this point, the power upon the Schmidt number will be less than 2/3. Therefore at Schmidt numbers less than unity a power dependency approaching ½ should be in evidence. Data for Schmidt numbers of about unity or less (for example 0.6 for air-water vapor) hardly provide a valid test; however Lynch and Wilke (*20*) recently presented data characterized by a Schmidt number of 0.24. Their careful analysis of these data revealed that the Schmidt exponent is close to ½. Indeed this fact was interpreted by Wilke (*31*) as perhaps being due to a concentration boundary-layer effect.

With respect to gas-liquid systems (for example absorption of a gas by a liquid flowing through a packed column) it might be expected that the Schmidt number exponent be 2/3 for the gas film, where a velocity gradient exists, and ½ for the liquid film, where for slight penetration the velocity gradient in the liquid film adjacent to the gas is probably negligible (*7*).

The foregoing remarks do not apply to transfer processes in turbulent flow, a topic which has been treated by Toor and Marchello (*29*).

CONCLUSIONS

The concept of diffusion within a boundary layer which is repeatedly developed and destroyed over a distance equal to one particle diameter is apparently supported by literature data for particle-fluid exchange in fixed beds. Additional research efforts are needed to provide data and interpretation at very low Reynolds numbers. Further studies are required in systems where the Schmidt number is significantly less than 1 to provide additional support for the contention that saturation of the hydrodynamic boundary layer results in a Schmidt exponent approaching ½.

It is possible that transfer rates in other systems, for example fluidized beds, might be interpreted in terms of an appropriately modified version of the boundary-layer model suggested here.

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NOTATION

a, b = exponents in velocity-distribution relation, Equation (3)
c = concentration of diffusing species
D = molecular diffusivity
D_p = particle diameter
j_D = mass transfer j factor
j_{BL} = j factor defined by Equation (14)
K = coefficient defined by Equations (3) and (10)
$\bar{k}$ = average mass transfer coefficient
n = number of particle diameters of length, Equation (17)
N_{Re} = Reynolds number, $D_p u_o/\nu\epsilon$
$N_{Re'}$ = Reynolds number, $D_p u_o/\nu$
N_{Sc} = Schmidt number
u = fluid velocity
u_o = superficial velocity
u_a = average velocity in a packed bed, $u_a = u_o/\epsilon$
u_∞ = velocity at boundary-layer edge
v = fluid-velocity component
x = distance in direction of flow
y = distance perpendicular to flow

Greek Letters

ϵ = fractional void volume
ν = kinematic viscosity
θ = time
π = 3.1416
Γ = gamma function

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Entrainment and Pressure Drop in Concurrent Gas - Liquid Flow: I. Air - Water in Horizontal Flow

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Experimental equipment and data are reported for entrainment and energy loss in annular, two-phase flow of water and air. Measurements were made with a sample withdrawal technique in 1- and 3-in. horizontal tubes. A knowledge of entrainment is necessary to an understanding of various mass transfer, heat transfer, and separation problems in two-phase flow. A preliminary correlation is presented.

Research in two-phase gas-liquid flow has increased steadily over the past ten years. In addition to a long-standing need for a better theoretical understanding of this type of flow the demands of a group of important industrial problems have accelerated this work.

Several investigators (*8, 17*) have demonstrated that when two phases flow together in a tube the liquid and gas streams can assume several different shapes. At high gas rates a predominant pattern is annular flow with the liquid at the wall and the gas moving in the core. This type of flow is thought to be accompanied by a dispersion or entrainment of part of the liquid in the gas phase. Entrainment is of considerable importance to an understanding of mass transfer, heat transfer, separation processes, and energy loss. This paper reports the first phase of a program to study entrainment. Equipment designed for direct measurement of entrainment and entrainment distribution is described. Experimental data on the air-water system is presented and preliminary correlation is proposed.

PREVIOUS STUDIES

Experimental data on entrainment or entrainment-measuring techniques in moving gas streams are very limited in the literature. Several studies of drop distribution from nozzles, spray chambers, and rotating disks (*16*) can be found. However in each of these cases the amount of liquid dispersed can be predetermined by the experimenter and the problems restricted to a study of drop-size distribution, spray areas, etc. In two-phase flow the entrainment is generated by the action

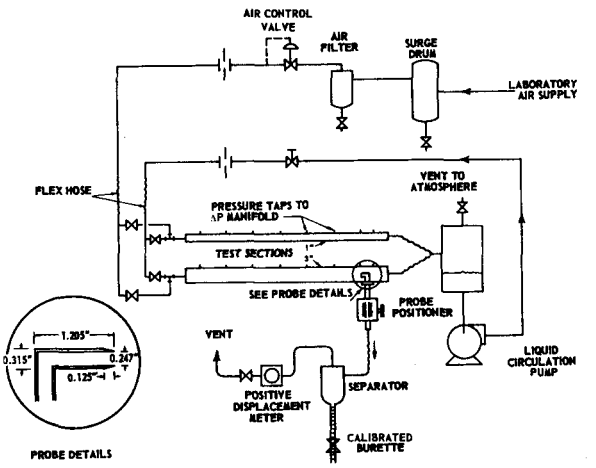

Fig. 1. Experimental equipment.