Mass Transfer in Packed Beds

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Although considerable work has been done on the problem of heat transfer radially in fixed beds through which gases are flowing, the data available for mass transfer are limited to one pipe size and one packing size and refer to average diffusivities for the entire bed. The present study was undertaken to determine: (1) diffusivities over a range of pipe and packing sizes and (2) the effect of radial position in the bed.

The measurements were made by introducing carbon dioxide into an air stream and analyzing the resultant mixture at various positions in the bed downstream from the point of injection. Pipe sizes of 2, 3, and 4 in. were packed with spherical particles of 5/32-, 1/4-, 3/8-, and 1/2-in. nominal diameter.

The differential equation describing the concentration in a packed bed when diffusivity E and the velocity u are permitted to vary with radial position was solved by use of an I.B.M. card-programmed calculator for the computations.

The results show that the Peclet number $D_p u/E$ increases from the center toward the wall of the pipe and that the increase is significant when D_p/D_t is greater than 0.05. Empirical correlations are then presented for both point Peclet numbers, which vary with radial position, and average Peclet numbers for the entire bed.

The variations in Peclet number with radius can be explained in terms of the corresponding variation in void fraction for 81% of the radius of the bed. At modified Reynolds numbers above 40 to 100 the equation $Pe = 8.0 + 100\ (\delta - \delta_o)$ correlates the effects of pipe and packing size and radial position. At radial positions greater than 0.81 wall friction influences turbulence conditions and the Peclet number.

In the design of fixed-bed catalytic reactors a knowledge of both heat and mass transfer rates in the radial direction is important. The heat transfer problem has received considerable attention, but data for mass transfer in gaseous systems are limited. The main objective of this study was to provide such information for a variety of tube and packing sizes.

Mass transfer is important not only in itself, but also because of its relation to the heat transfer process which occurs simultaneously under the influence of the temperature gradient existing radially in the packed bed. Although the mass transfer process takes place primarily by the mechanism of convection, heat transfer can occur by a variety of other mechanisms also. Hence a study of mass transfer provides a means of breaking down the more complex heat transfer process, at least partially, into its component parts.

Previous heat transfer studies (*1, 10*) have indicated that effective thermal conductivities vary with radial position. Since it seemed likely that effective diffusivities would also show such variations, a further purpose of this study was to determine point values of the diffusivity at different positions in the bed.

Because of the possible variation in both diffusivity and velocity with radial position, a complex differential equation must be used to relate the variables. One method of handling the problem is to obtain data at a number of packing-bed depths and solve the equation for the diffusivity, or Peclet number, by differentiating the data rather than integrating the equation. This procedure has been used in attacking the analogous heat transfer problem(*10*). To eliminate both the necessity for measuring concentrations at multiple bed depths and the errors associated with graphical differentiation, in the present study the complex equation was solved with the aid of an I.B.M. card-programmed calculator. Hence another purpose of the study was to demonstrate the use of an automatic computing ma-

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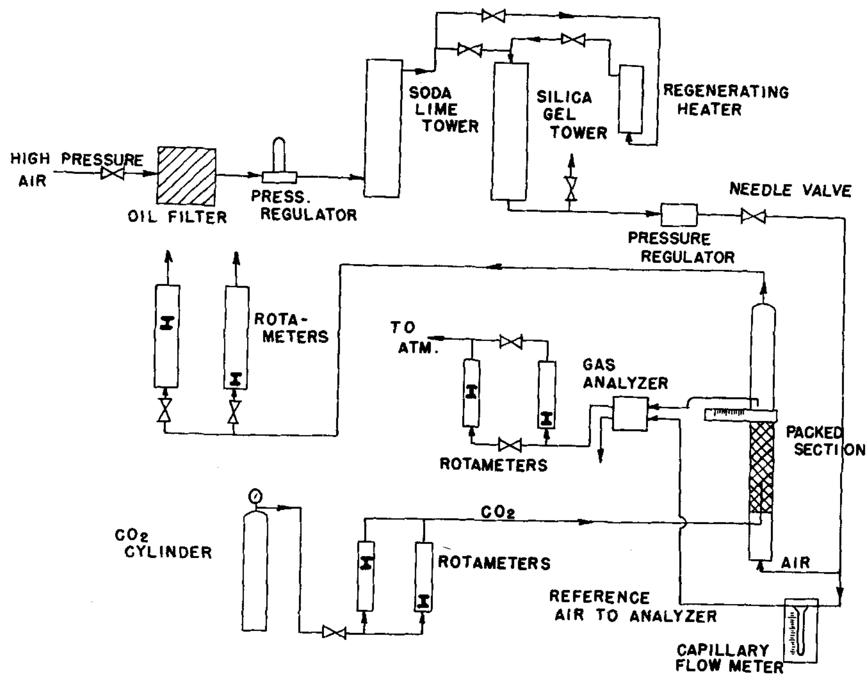

FIG. 1. FLOW SHEET OF AIR–CARBON DIOXIDE SYSTEM.

chine in chemical engineering calculations of this type. The details of setting up such calculations on the C.P.C. machine will be described in a separate paper.

The experimental technique consisted of injecting carbon dioxide into an air stream flowing through the vertical packed bed. At some height above the point of injection, samples of the air–carbon dioxide mixture were withdrawn and analyzed. A knowledge of the concentration and velocity [available from Schwartz and Smith(*11*)] across the diameter of the bed at a single bed depth provided sufficient information to yield effective diffusivity values at any point in the bed.

PREVIOUS WORK

The first measurements of mass transfer by turbulent diffusion in gaseous systems were carried out by Sherwood and Towle(*14*). Although their work was done in an empty pipe, the results are important for fixed-bed diffusion, as it was shown that the diffusivity was not influenced by the molecular weight of the diffusing component.

Bernard and Wilhelm(*3*) reported considerable data on radial mass transfer rates in liquid systems and also the only published values for gaseous systems, i.e., for carbon dioxide diffusing across an air stream flowing through an 8-in. diam. pipe packed with 3/8-in. spheres.

Singer and Wilhelm(*13*) have assembled data on heat and mass transfer in terms of the Peclet group, Reynolds number, and the ratio of particle-to-tube diameter. These results show that the Peclet group for heat transfer is generally smaller than the corresponding group for mass transfer.

From theoretical considerations Baron(*2*) has predicted that the Peclet number should be between 5 and 13. The basis for this prediction is the random-walk theory, in which a statistical approach is employed. Latinen(*7*) has extended the random-walk concept to three dimensions and demonstrates the applicability of his theory to a body-centered cubic packing arrangement. For fully developed turbulence a Peclet number of 11.3 is predicted. These methods of prediction do not take into account effects of radial variations in velocity and void space.

Ranz(*8*), postulating a different orientation in the bed and also assuming that the Peclet number does not depend upon the velocity or void space, proposed another method of prediction. When applied to a system of spherical particles, packed with their centers at the corners of tetrahedrons, this approach gives $Pe = 11.2$.

The availability of data showing the variation of void fraction with radial position(*9*) makes possible a clearer interpretation of the present mass transfer study.

SCOPE OF WORK

The following variables were studied:

Pipe size: 2, 3, 4 in.

Mass velocity: 125, 250, 500, 1,000 and 1,500 lb./(hr.) (sq. ft. of total pipe area). In some cases 40, 775, and 1,500 values were also used.

Packing size: 5/32-, 0.30-, 0.36-, and 0.58-in. spheres.

For each combination of the foregoing variables, three diameters across the bed were traversed, and between twenty-four and fifty-one samples of carbon dioxide were taken and analyzed. The range of modified Reynolds numbers was from 12 to 1,180, and the range of particle-to-tube diameter, D_p/D_t, from 0.038 to 0.175.

APPARATUS AND EXPERIMENTAL PROCEDURE

Figure 1 shows a schematic diagram of the entire apparatus, consisting of an air-cleaning and purifying section, an air-metering section, the test section, a carbon dioxide metering section, and a gas-analyzing section.

Carbon dioxide and water vapor were removed from the incoming air by soda lime and silica gel towers.

The test section in detail is shown in Figure 2. Straightening vanes were inserted just above the elbow leading into the section. The carbon dioxide injection tube entered the section above the straightening vanes and passed through a wire screen supporting the packing. In the 2-in. pipe runs, the 0.135-in. I.D. injection tube terminated at a point 23 in. above the screen. The upper tip of the tube was ground to a thin edge. In the 3-in. pipe runs, a 0.183-in. I.D. injection tube was used, and its tip extended 13.5 in. above the screen holding the packing. For the 4-in.-

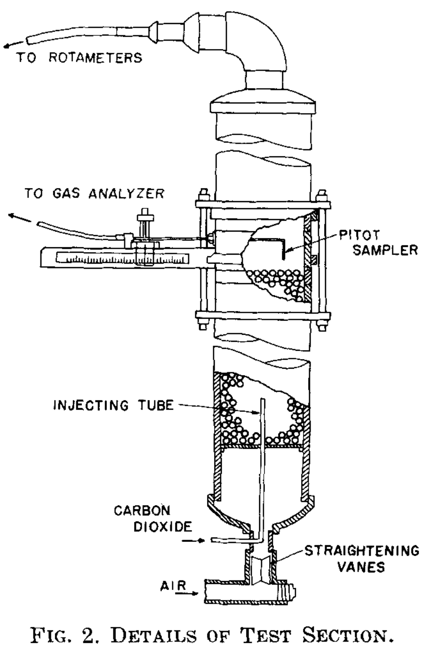

FIG. 2. DETAILS OF TEST SECTION.

pipe setup, the 0.183-in. injection tube extended 10.6 in. above the screen.

The height of packing above the tip of the injection tube was varied in the 2-in.-pipe runs, but the final data were taken at a height of 9 1/2 in. for the 5/32-in. spheres and 6 3/8 in. for the 3/8-in. spheres. The corresponding values for the 3- and 4-in.-pipes were 9.6 and 12.4 in. A statistical analysis, described in the next section, was used to arrive at these bed heights.

The bed was packed by pouring the spheres slowly from the top, using a rotating motion. This normal packing, as described by Furnas (*4*), was found to give more reproducible results than methods involving tapping. A similar conclusion was reached by Schwartz and Smith(*11*) in their velocity investigation.

Samples of carbon dioxide were removed from the top of the packed bed through a 1/16-in. O.D. Pitot tube. The tube was housed in a brass ring (Figure 2) that permitted samples to be taken from any radial position and across any diameter of the pipe.

The samples were passed through one side of an M/T-T-8 thermal-conductivity analyzer, supplied by the Gow-Mac Company. Reference air for this instrument was taken from a point just before the bed so that the measured values represented differences in concentration between the point in the bed and the inlet air.

The M/T-T-8 analyzer is an eight-filament unit containing two cells in each of four arms of a Wheatstone's bridge circuit. A constant bridge current of 100 ma. was supplied from lead storage batteries. The unbalanced e.m.f. from the bridge circuit was measured and recorded on a Leeds and Northrup Model *S* Micromax. The difference between the chart readings when a sample was passing through one cell and when reference air was in both cells was a measure of the concentration of the sample.

The flow rate through the sampling cell was fixed at a value such that the velocities inside and outside the sampling tube were the same. A number of special experiments were made to determine how rapidly samples could be withdrawn without causing appreciable mixing, and optimum values were obtained for each set of conditions.

Likewise the carbon dioxide was admitted at a speed designed to maintain an undisturbed velocity profile within the bed. This average velocity in the injection tube was found by experiment to be approximately the same as in the test section.

The analyzer was calibrated by preparing mixtures of air and carbon dioxide by use of the rotameters in the apparatus for a measure of the concentration. In order to increase the accuracy of the calibration, all concentrations were referred to a reference value, C_A, which was the measured average effluent concentration from the test section. The calibration curve could then be expressed by the equation.

$$\frac{\Delta Y}{\Delta Y_A} = \left(\frac{C}{C_A}\right)^{1/b} \tag{1}$$

where ΔY refers to the difference in chart reading and b is the calibration constant. The use of the effluent concentration as the reference value minimized errors due to temperature changes and similar variables which might change from day to day. In substance this procedure amounted to checking one point on the calibration curve with each run.

Pellet sizes were measured by two methods: (1) measuring the diameter of several units with a micrometer and (2) measuring the volume of water displaced by approximately 100 units and computing the diameter equivalent to a perfect sphere. The 5/32-in. steel balls were nearly uniform with an average diameter of 0.156 in. The 1/4-, 3/8-, and 1/2-in. particles were alumina-catalyst-support pellets and were somewhat irregular spheres. Their actual average diameters were 0.30, 0.36, and 0.58 in.

STATISTICAL ANALYSIS AND REPRODUCIBILITY

Reproducibility. Concentrations measured in a packed bed are subject to large variations from point to point as a result of the random packing distribution within the bed. Hence samples removed from points on different radii, but at the same radial position, r/r_o, will be distributed randomly about a mean concentration which is characteristic of that radial position. The extent of the variations which occur are shown in Figure 3, where concentration ratios, C/C_A, at constant radial position are plotted vs. an angular position corresponding to the diameter traversed.

In view of these results and since the effect of radial variation on Peclet number was an objective, it was deemed necessary to measure carefully concentrations over a number of diameters. To carry out this program most efficiently a statistical analysis of typical sets of data was undertaken. The results from four runs (4,141, 4,142, 4,143, and 2,141) made in the 2-in. pipe with 5/32-in. packing were employed and measurements were made at a packing-bed depth of 8.13 in. (above the injector-tube tip) and across three diameters 120° apart. The results are plotted in Figure 4. The deviations from the mean range from 3% at the center to 2.5% at the wall.

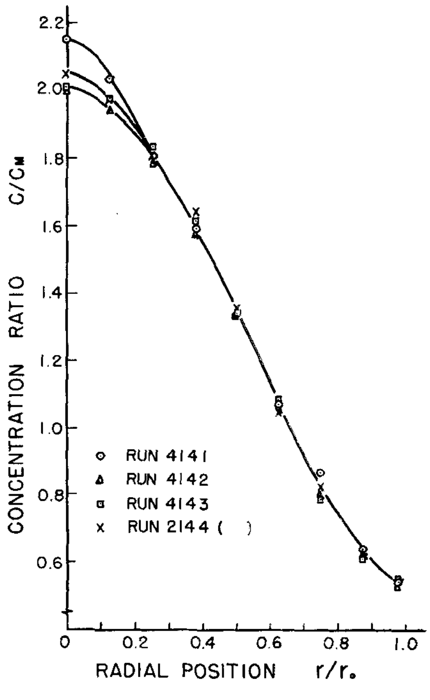

FIG. 4. REPRODUCIBILITY OF CONCENTRATION PROFILES, 2-IN. TUBE, 5/32-IN. SPHERES.

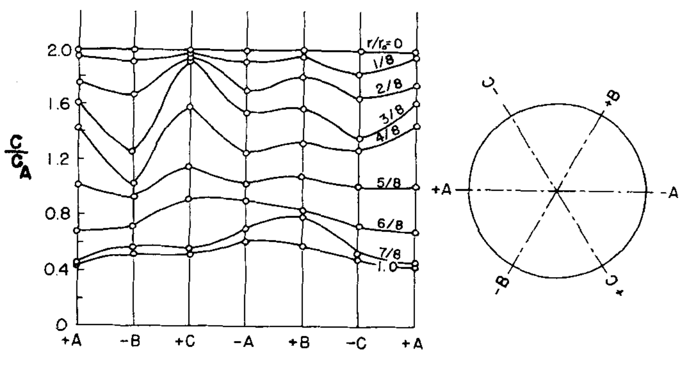

FIG. 3. VARIATION OF CONCENTRATION WITH RADIAL AND ANGULAR POSITION, 8.09-IN. BED DEPTH.

Effect of Repacking the Bed. An analysis of variance using the data in Figures 3 and 4 showed that the error resulting from taking data over three different diameters was not significantly different from that of taking data over one diameter and repacking the bed three times. Hence all data were obtained over three diameters with but one bed packing for each set of conditions.

Effect of Bed Height. At low heights of packing, errors would be expected owing to the presence of the injector tube. On the other hand, the concentration profile flattens out at high bed depths and introduces errors in the analysis of the data. Hence an optimum packing height exists for each set of conditions. To test these factors, Kurihara(*6*) has measured concentration profiles for packing depths ranging from 1.69 to 11.03 in. for 5/32-in. pellets in the 2-in. pipe. The data are shown in Figure 5 and the computed Peclet numbers in Figure 6. The fact that the graphical differentiation technique was used to obtain the Peclet numbers explains some of the variation in the values; however it is clear that at bed heights above 6 in. the effect of bed height is not large in comparison with random errors due to packing distribution. On the basis of these data were determined the bed heights given in the section on Apparatus.

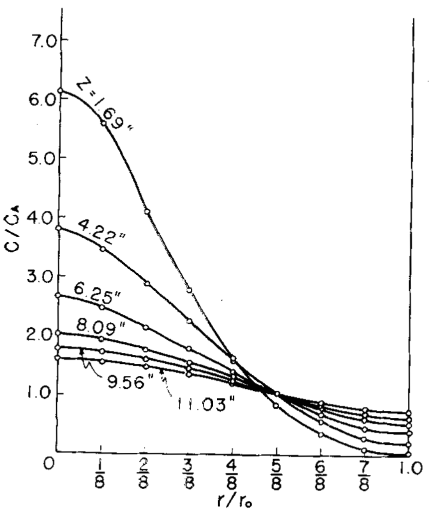

FIG. 5. VARIATION OF CONCENTRATION WITH RADIAL POSITION.

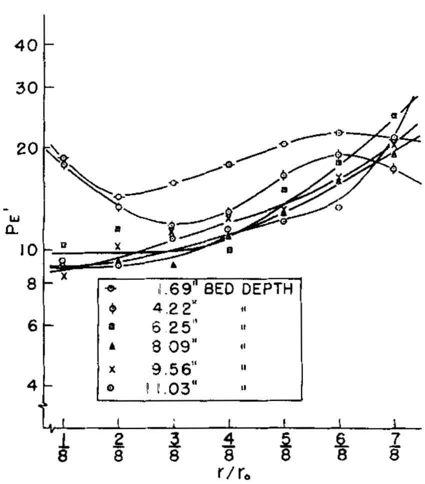

FIG. 6. VARIATION OF MODIFIED *Pe* WITH RADIAL POSITION OBTAINED BY THE GRAPHICAL METHOD.

Error in Carbon Dioxide Analysis. The statistical analysis showed that differences between diameters were significant at the 5% confidence level when compared with the residual variation. The randomness of the packing therefore was the primary cause of the differences between different sets of data, such as shown in Figure 4, and not errors in carbon dioxide analysis and errors due to other assignable causes.

Since the effluent concentration was measured for each run, it is possible to compare this value with the integrated average concentration. This comparison however involves more than the error in the carbon dioxide analysis, for the velocity data of Schwartz and Smith(*11*) must be employed in obtaining the integrated value. For all the data the deviation between the two quantities averaged 4.8%. It is worth while to note that assuming a uniform velocity profile rather than using the available data would have led to much greater deviations between the integrated and measured average concentrations. It is believed that the 4.8% value represents the degree of correspondence between the velocity and concentration measurements which were made with the same packing materials but in different equipment.

Effect of Height of Pitot Tube above Top of Bed. In taking samples from the top of the packed bed, it was important that random variations were minimized so that average concentrations might be obtained from a minimum amount of data; hence it was not desirable to withdraw samples from directly above the packing. On the other hand, experiments indicated that appreciable mixing occurred if the distance above the packing became great. On the basis of several trial runs it was decided that a distance above the packing of 1/4 to 1/2 in. represented the optimum condition, and this spacing was used in taking the final data.

The velocity data of Schwartz and Smith(*11*), used in analyzing the results of the present investigation, were obtained at a height of 2 in. above the top of the packing. This larger distance was necessary because of the hot-wire–anemometer technique employed to measure velocities. At distance of 1/4 to 1/2 in. velocity components perpendicular to the direction of flow affected the anemometer readings. It was found that if the distance was increased to 2 in., these velocity components were negligible, and the velocity in the direction of flow still was not affected by the empty pipe length of 2 in. In the concentration measurements, perpendicular velocity components were of no significance, and so accurate data could be obtained by sampling the gas at the much smaller distances of 1/4 to 1/2 in. above the packing.

CALCULATION OF RESULTS

Development of Equation. It is usually assumed that a differential equation can be written to describe the temperature and concentration in a packed bed, an assumption that presupposes that it is possible to choose a differential element large enough to represent average conditions over an area involving both packing and void space, yet small enough to assume continuity of temperature and concentration gradients. This approach therefore assumes that heat and mass transfer are occurring continuously and uniformly across each radius of the packed bed. The actual process takes place to a large extent in the form of discrete displacements controlled by the dimensions of the packing. Under these conditions it can be argued that the abstraction of a differential equation need not be employed to describe processes occurring in finite steps but that these processes might better be described in terms of difference equations which could be solved numerically with high-speed computing equipment.

Although such an argument has much to recommend it, the past development of reactor-design methods and treatment of heat transfer data has been entirely in terms of the differential-equation approach. Accordingly, in this present study the differential equation for mass transfer has been used as a starting point, although its solution has been obtained by substitution of difference equations and with the aid of computing machines. Thus the concept of an effective diffusivity, E, has been retained as defined by the expression

Rate of mass transfer per unit

$$\text{area} \qquad = -E\frac{dC}{dr} \qquad (2)$$

Under these conditions the basic differential equation for mass transfer in the bed may be written

$$\frac{\partial\left(Er\dfrac{\partial C}{\partial r}\right)}{\partial r} = r\frac{\partial\ (Cu)}{\partial z} \qquad (3)$$

This expression is based upon two additional assumptions besides Equation (2); i.e., (1) angular symmetry is everywhere present, and (2) diffusion in the axial direction can be neglected. Axial diffusion is probably unimportant at all except the lowest mass velocities because the mass transfer due to the bulk velocity of the gas is predominant. It is not possible to introduce an accurate longitudinal term in the differential equation because of inadequate knowledge of the diffusivity in the axial direction.

Schwartz and Smith (*11*) have found that the variation of velocity u with bed height is not large compared with random variations at a given radial position. With this simplification, and introducing the radial position coordinate $\theta = r/r_o$, Equation (3) becomes

$$\frac{\partial\left(E\,\theta\dfrac{\partial C}{\partial\,\theta}\right)}{\partial\,\theta} = r_o^2 u\,\theta\frac{\partial C}{\partial z} \qquad (4)$$

The boundary conditions are

$$\left(\frac{\partial C}{\partial\,\theta}\right)_{\theta=0} = 0 \text{ angular symmetry} \qquad (5)$$

$$\left(\frac{\partial C}{\partial\,\theta}\right)_{\theta=1} = 0 \text{ no mass transfer at wall} \qquad (6)$$

$$\begin{array}{ll} C(\theta,\,0) = C_f & 0 < \theta < t \\ C(\theta,\,0) = 0 & t < \theta < 1 \end{array} \qquad (7)$$

Boundary condition (7) represents the physical situation at zero bed depth where pure carbon dioxide of concentration C_f is introduced into the bed through an injection tube of radius tr_o.

Solution of Equation. Equation (4) cannot be solved analytically unless the relationship between the diffusivity E and the radial position r is known. Since this was one objective of the work, numerical methods had to be used. It may be noted that if both E and u are assumed constant the coefficients are constant and an analytical solution in terms of Bessel functions is possible.

Point values of the diffusivity and the Peclet number at various radial positions were obtained by using the available velocity data (*11*) and replacing Equation (4) with a set of homogeneous linear difference equations which could be solved with the aid of an I.B.M. card-programmed calculator.

The general method of solution can be outlined as follows:

1. It is postulated that the concentration C can be considered the product of two functions R and Z, the first of which is a function of r only and the second a function of z only. Two ordinary differential equations are obtained: one involving Z and one involving R.
2. The equation containing Z is solved analytically by ordinary methods.
3. The equation involving R is a complex differential equation whose analytical solution, if possible, would be extremely difficult. This equation may be replaced by a system of difference equations, each written about a point in the region from $r = o$ to $r = r_o$.
4. This system of difference equations is actually a set of homogeneous linear equations involving the values of an eigen function on R at each interval in the region and an eigen value, λ.
5. This set of linear equations can be solved by trial and error for values of R and λ at each radial position by use of the velocity and concentration

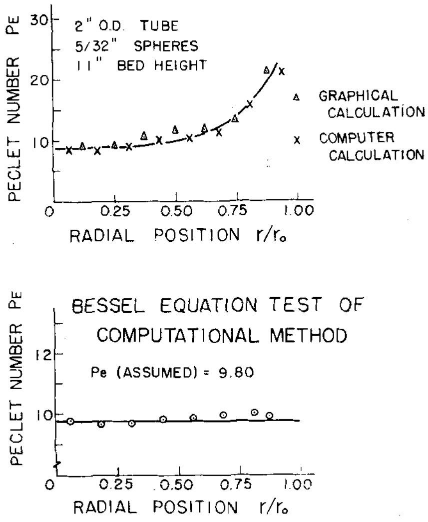

FIG. 7. COMPARISON BETWEEN MACHINE AND GRAPHICAL CALCULATION.

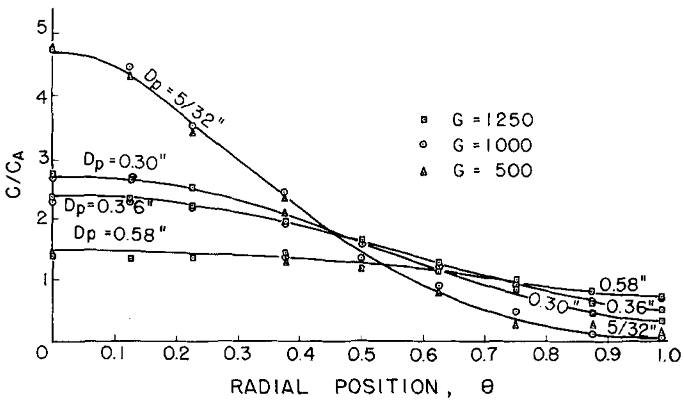

FIG. 8*a*. VARIATION OF CONCENTRATION WITH RADIAL POSITION, 4-IN. PIPE.

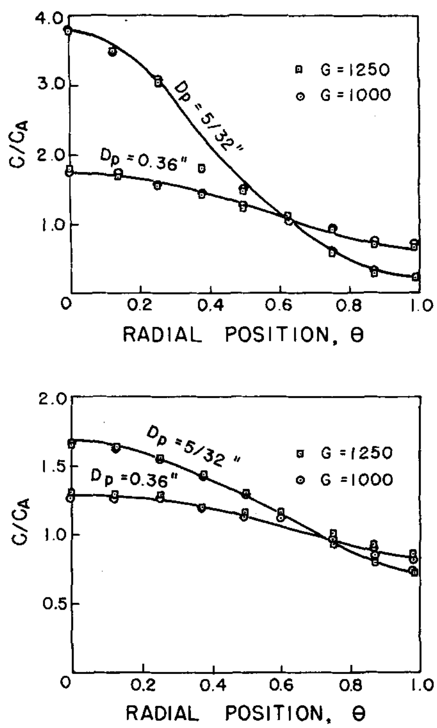

FIG. 8*b*. CONCENTRATION VS. RADIAL POSITION; 3-IN. PIPE ABOVE, 2-IN. PIPE BELOW.

data. The form of the solution is

$$C = \sum_{0}^{n} A_n R_n \ exp \ (-4\lambda_n^2 z/D_t^2) \quad (8)$$

where A_n are constants, R_n are the eigen functions depending upon radial position only, and λ_n are the eigen values determined by the boundary conditions.

The procedures for carrying out the calculations on the I.B.M. machine are described in a separate paper.

The measured concentration data across three diameters of the pipe gave six individual values at each radial position. These were averaged arithmetically to obtain the mean concentration used in the calculations. The diameter of the pipe was divided into eight intervals, so that Peclet numbers were obtained at values of θ equal to 1/16, 3/16, 5/16, 7/16, 11/16, and 13/16 and 15/16.

To test the computation method the Bessel Test was carried out; that is, the velocity and diffusivity were assumed constant, and an arbitrary value of the Peclet number of 9.8 was chosen. Then the concentration profile for this hypothetical case was obtained from the Bessel solution. These concentrations were used in the computation method to compute Peclet numbers at each radial position. If there is no error in the method, the value of Pe should be 9.8 in each case.

The results of the test are shown in the lower half of Figure 7 and indicate the validity of the method. In the upper part of the figure is a comparison of Peclet numbers computed graphically by Kuriahra (*6*) and by the computational method.

For some purposes, particularly simplified reactor-design procedures, average values of the Peclet number across the entire diameter of the bed are useful. Various methods might be used to obtain such results. Bernard and Wilhelm (*3*) assumed that both velocity and eddy diffusivity were constant and used a Bessel solution of Equation (4) to obtain mean Peclet numbers. Another assumption is that the ratio u/E is constant. This second approach was used in this work and Equation (4) again solved with the C.P.C. machine to obtain average values of Pe.

The values of the velocity u used in the calculations and the values of E computed are based upon the superficial area, rather than on an area determined from the actual void fraction.

TABLE 2.—AVERAGE VALUES OF PECLET NUMBER, $D_p u/E$

Tube size, in.	Pellet size, in.	Mass velocity, lb./(hr.) (sq. ft.)						
		40	125	250	500	1000	1250	1500
4	5/32	6.00	12.3	9.86	7.80	8.42		
4	0.30	....	8.68	9.30	8.55	8.80	8.48	
4	0.36	9.67	9.67	....	9.00	9.43	9.90	
4	0.58	....	11.2	11.1	12.7	12.7	12.9	
3	5/32	....	9.35	9.58	8.13	8.41	8.27	
3	0.36	....	11.6	10.5	9.50	9.88	9.78	
2	5/32	....	10.7	10.7	10.1	10.1	....	10.0
2	0.36	....	13.5	12.3	12.1	12.9	....	13.0

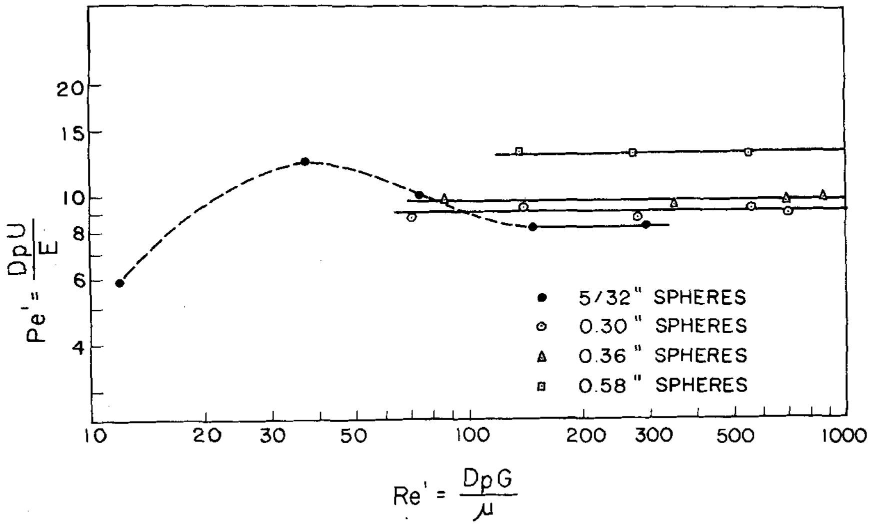

FIG. 9. AVERAGE PECLET NUMBER CALCULATED BY METHOD A (CONSTANT U/E), 4-IN. PIPE.

TABLE 4.—POINT VALUES OF PECLET NUMBER, $D_p u/E$

G = 125 lb./(hr.) (sq. ft.)

Radial position	2-in. Pipe		3-in. Pipe		4-in. Pipe			
	5/32 in.	0.36 in.	5/32 in.	0.36 in.	5/32 in.	0.30 in.	0.36 in.	0.58 in.
3/16	9.3	9.0	7.0	9.4	7.0	9.3	7.8	8.1
5/16	8.3	10.5	8.5	10.2	8.0	8.0	7.8	8.2
7/16	8.9	11.1	10.8	9.8	8.1	8.2	7.6	7.6
9/16	9.2	13.2	11.7	9.6	10.3	9.2	10.6	11.7
11/16	11.0	16.3	11.7	11.0	9.9	11.3	16.7	14.9
13/16	12.8	24.2	12.3	13.4	9.9	21.2	22.6	18.5
15/16	32.2	36.5	14.0	38.5	10.9	35.0	38.1	44.3

RESULTS

The measured concentration ratios, shown as mean values with respect to angular position, are presented in Table 1*. Typical concentration profiles across the radius of the bed are shown for the 4-in. pipe in Figure 8*a* and for the 2- and 3-in. pipes in Figure 8*b*. It is interesting to note that the concentration does not vary with mass velocity in the range covered by the graph.

Average values of the Peclet number, computed on the assumption that u/E does not vary with radial position, are given for all conditions in Table 2, and in Figure 9 for the 4-in. pipe. Because the concentration profiles are nonvariant with mass velocity, it is seen from Figure 9 that the Peclet

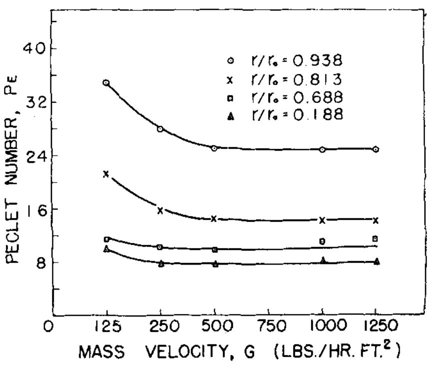

FIG. 10. EFFECT OF MASS VELOCITY ON PECLET NUMBER, 4-IN. PIPE, 0.30-IN. SPHERES.

*Tables 1 and 3 are on file with the American Documentation Institute, Auxiliary Publications Photoduplication Service, Library of Congress, Washington 25, D. C., and may be ordered as document 4475 on remission of $1.25 for microfilm or photoprints.

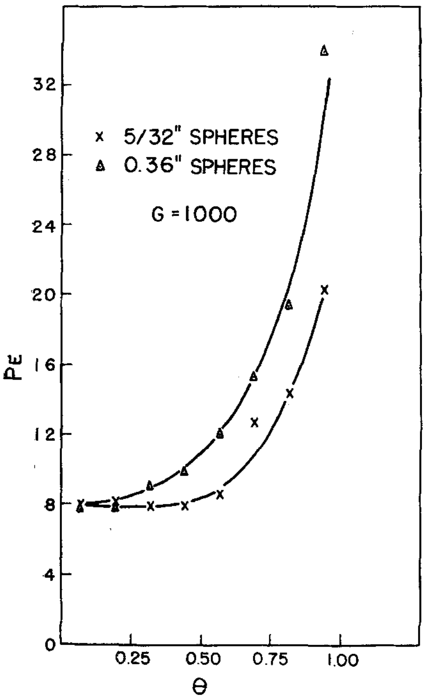

FIG. 11. PECLET NUMBER IN A 2-IN. PIPE.

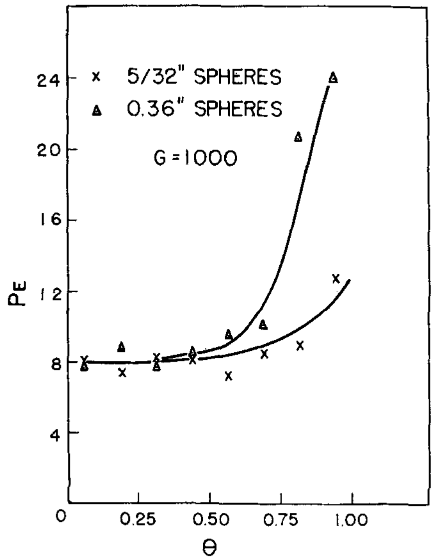

FIG. 12. PECLET NUMBER IN A 3-IN. PIPE.

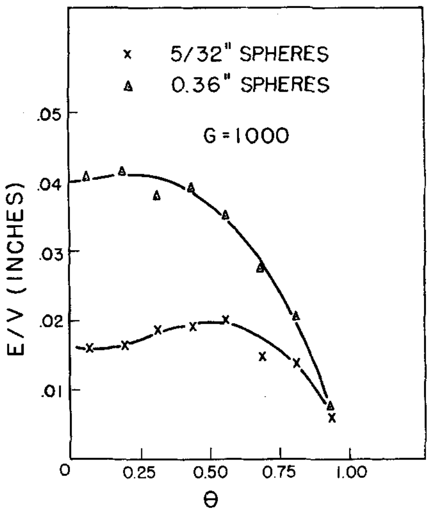

FIG. 14. EFFECTIVE DIFFUSIVITY IN A 2-IN. PIPE.

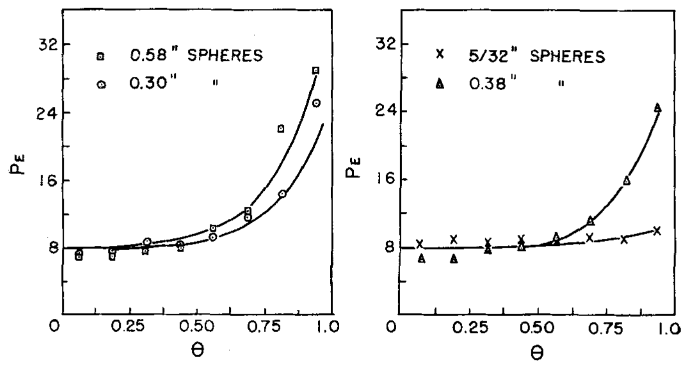

FIG. 13*a* AND *b*. PECLET NUMBER IN A 4-IN. PIPE.

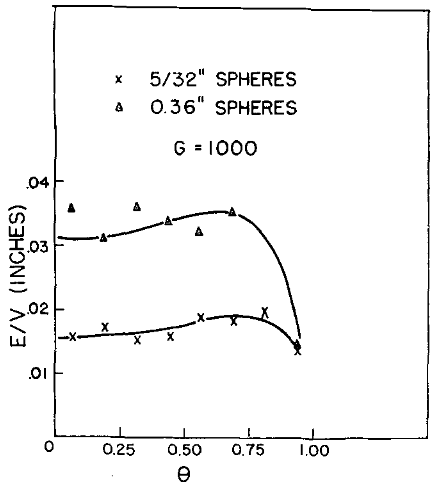

FIG. 15. EFFECTIVE DIFFUSIVITY IN A 3-IN. PIPE.

numbers are also essentially constant above $G = 500$ lb./(hr.) (sq. ft.).

Point values of the Peclet number also show little variation with mass velocity at the higher levels, as indicated in Figure 10 for 4-in.-pipe data. In Table 3* are shown point Peclet numbers for mass velocities above 500 lb./(hr.) (sq. ft.). Table 4 gives the results at 125 lb./(hr.) (sq. ft.).

DISCUSSION OF RESULTS

A quantitative explanation of diffusion on a theoretical basis is difficult because the problems involved are so closely connected with fluid dynamics. A satisfactory theory of fluid dynamics for a packed bed has not been developed. The theories of Prandtl, Von Karman, and Taylor, which have been applied in simple cases of homoge-

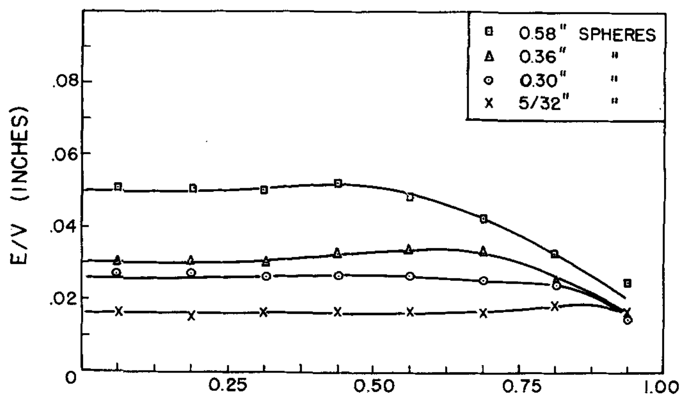

FIG. 16. EFFECTIVE DIFFUSIVITY IN A 4-IN. PIPE.

* See footnote on page 33.

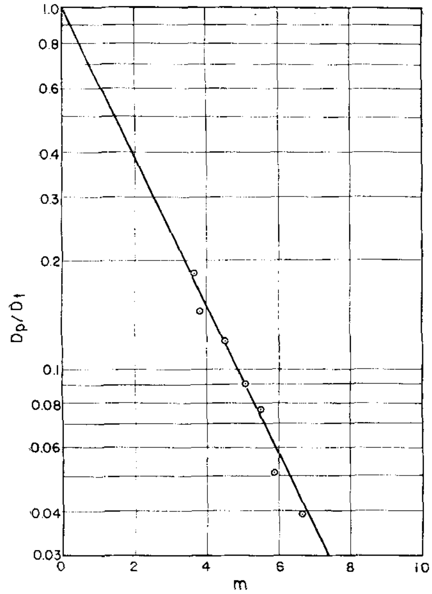

FIG. 17. CORRELATION OF m WITH D_p/D_t.

neous flow, are difficult to extend to packed beds because of the random arrangement and sizes of the channels and the numerous irregularly arranged surfaces. Hence a sound theoretical interpretation of the variation of Peclet number with radial position does not seem possible at present; nevertheless, a method of predicting Peclet numbers from the known bed parameters is important in reactor-design problems. Accordingly, first are presented empirical equations which correlate the data obtained, and then in the next section the theoretical implications, particularly with respect to void space, are considered. The interpretation of the data is aided by the availability of velocity (*11*) and void fraction (*9*) information for the same bed conditions.

Correlation of Point Peclet Numbers. Perhaps the most important result of this study is the significant increase of the Peclet number with an increase in radial position, an increase that depends upon the ratio D_p/D_t and is significant when the ratio is above about 0.05. These conclusions are evident from Figures 11, 12 and 13. For the 5/32-in. particles in the 4-in. pipe ($D_p/D_t = 0.038$) the Peclet number profile is almost flat (*see* Figure 13). At the other extreme, Figure 11, the increase in Peclet number begins at the center of the pipe. The value of Pe at the center in all cases is essentially 8.0.

A second interesting result is that values of the eddy diffusivity for different particle sizes are different near the center of the pipe but similar as the wall is approached. This is seen in Figures 14, 15, 16, where the eddy diffusivity divided by the average velocity, V, over the whole pipe is plotted vs. radial position. At the center the diffusivity is proportional to the particle size, but near the wall it is largely determined by the tube size.

Mathematically these conclusions regarding the Peclet number can be represented by an expression of the form

$$Pe = Pe_o + F\ \theta^m \qquad (9)$$

where F and m depend upon particle and tube sizes and Pe_o is the value of the Peclet number at the center of the tube and is equal to 8.0. Values of m and F were obtained from Equation (9) and the tabulated values of Pe. The resulting correlations for F and m in terms of D_p/D_t are shown in Figures 17 and 18. These two graphs, along with Equation (9), correlate all the data at mass velocities above $G = 500$ lb./(hr.) (sq. ft.) within 10%. Values of the Peclet number at lower mass velocities are higher, as indicated by Figure 10, but the increase is only of the order of 10 to 20%.

Equation (9) predicts a continual increase in Peclet number as D_p/D_t is increased and a value of 108 may be estimated for an empty tube ($D_p/D_t = 1.0$) by logarithmic extrapolation. This is in reasonable agreement with Sherwood and Towle's result of 118 $(Re)^{0.1}$, considering the extrapolation involved.

Correlation of Average Peclet Numbers. The effect of particle size on average Peclet numbers can be correlated by a function involving $(D_p/D_t)^2$. The result is shown in Figure 19. The data of Bernard and Wilhelm, obtained assuming E and u were constant, are also included.

THEORETICAL CONSIDERATIONS

It has been mentioned that the random-walk theory has been applied to packed beds (*2, 7*). This is essentially an extension of the

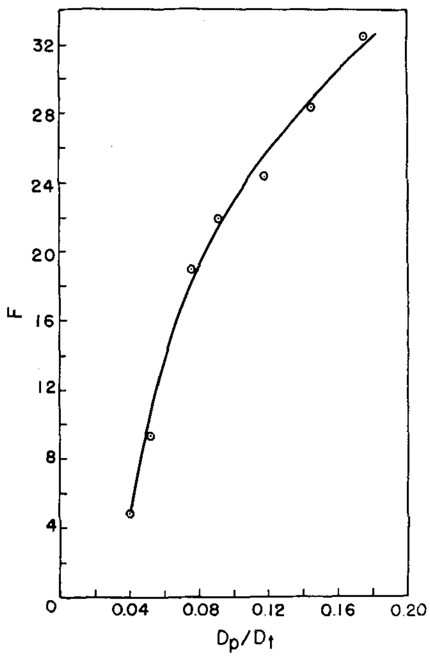

FIG. 18. CORRELATION OF F WITH D_p/D_t.

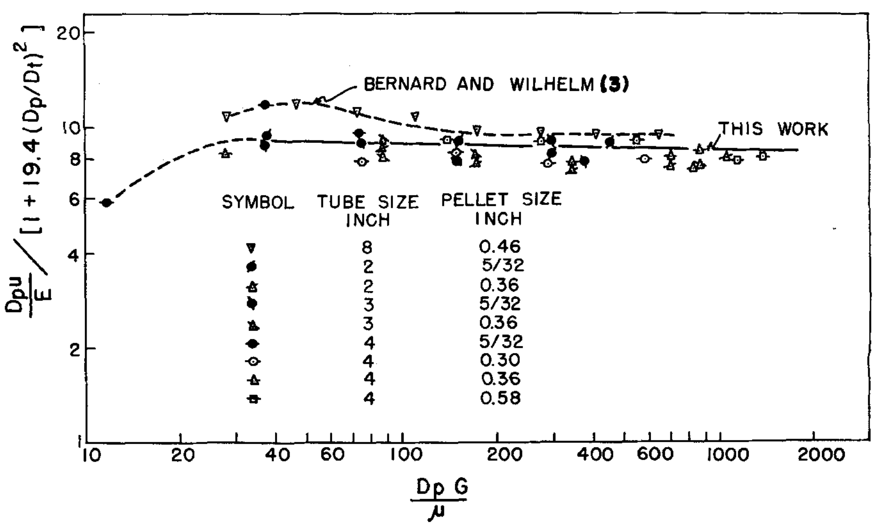

FIG. 19. CORRELATION OF AVERAGE PECLET NUMBER WITH D_p/D_t AND REYNOLDS NUMBER.

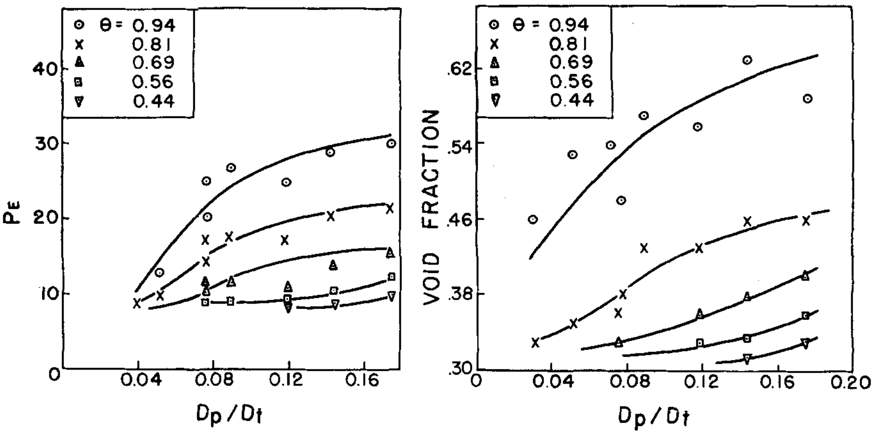

FIG. 20. LEFT: EFFECT OF D_p/D_t ON PECLET NUMBER; RIGHT: EFFECT OF D_p/D_t ON VOID FRACTION.

Einstein equation for diffusion in Brownian motion. Taylor (5) originally applied the concept of a relationship between the eddy diffusivity and the mean-square lateral displacement to homogeneous fluid systems. Baron's (2) and Latinen's (7) developments are logical extensions to packed-bed arrangements. The radial displacement of the fluid stream in a bed is determined largely by the dimensions of the channels, which are themselves randomly arranged. The application of the Einstein equation to the process requires the following chief assumptions: (1) mixing within each interstice is substantially complete so that a fluid element within a void has an equal probability of leaving by any of several exit paths; (2) the number of radial displacements is sufficiently large that statistical principles may be employed to estimate the mean-square displacement; and (3) effects due to changes in void fraction, velocity variations, and presence of the tube wall are neglected.

From assumption (3), the theory would be expected to be successful in predicting the point values of the diffusivity at the center of almost any packed-tube arrangement, and also the point values across the entire diameter when D_p/D_t is small. Such is indeed the case, for the value of $Pe = 8.0$ at the center of the bed, determined in this study, is almost midway between the limits of 5 and 13 predicted by Baron. Also, where D_p/D_t is small, as in the lower curve of Figure 13*b*, the entire range of Peclet numbers is within the prediction interval. These conclusions are sound as long as the mass velocity is sufficiently high to make assumption (1) valid. As the mass velocity is decreased, the Peclet number will first increase as the effect of incomplete mixing becomes significant and finally decrease to zero at zero velocity where molecular diffusion is the controlling factor. This maximum in the Peclet number is illustrated in Figure 9 and also to a slight extent in the average Peclet numbers shown in Figure 19. It is not valid to postulate a critical Reynolds number at which the Peclet number becomes dependent upon mass velocity, because the particle diameter and void fraction are also factors which affect this transition. However from the available data it appears that Reynolds numbers from 40 to 100 constitute the critical range.

Effect of Void Fraction and Pipe Wall. Returning to the variation in Peclet numbers with radial position, it seems clear that the fundamental factors involved are the void fraction and the influence of the pipe wall. A comparison of the radial variation in both void fraction (9) and Peclet number as presented in Figure 20 is striking.

The similarity in shape of the two sets of curves lends substance to the belief that internal changes in void space have a large effect on the Peclet number. However, void-space changes cannot explain the variation in Peclet number over the entire pipe radius. Near the wall, tube-generated turbulence becomes important with respect to particle-generated turbulence, and this has its effect on the Peclet number.

These conclusions are shown graphically in Figure 21, where the increase in Peclet number above the value at the center of the tube is plotted vs. the corresponding increase in void fraction. Up to a radial position of 0.81 the Peclet number is proportional to the void fraction; hence for 81% of the pipe radius the empirical correlation of Equation (9) in terms of radial position and D_p/D_t can be replaced by the more fundamental relation

$$Pe = 8.0 + 100\,(\delta - \delta_o) \quad (10)$$

(limited to $\theta < 0.81$ and $Re > 100$) in terms solely of void fraction δ.

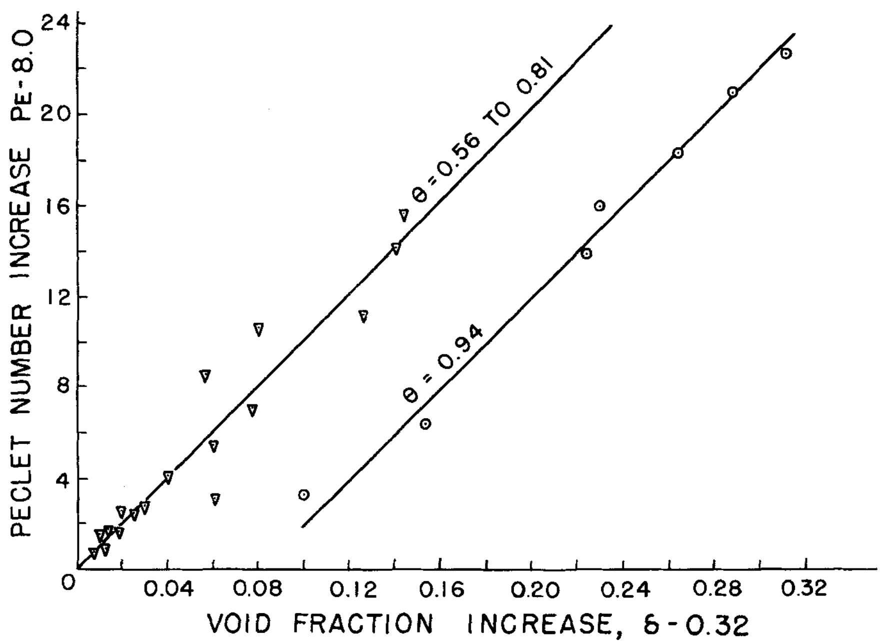

FIG. 21. EFFECT OF VOID FRACTION ON PECLET NUMBER.

The effect of the tube wall is also evident from Figure 21, where the line for a radial position of 0.94 is seen to be displaced from that for θ from 0 to 0.81. At this radial position near the wall the velocity is decreasing rapidly owing to wall friction. Hence the void fraction alone is not sufficient to describe the turbulence conditions and therefore the Peclet number.

Explanation in Terms of Existing Theories. The increase in Peclet number can be qualitatively considered by modification of the random-walk concept, as extended by Latinen. This theory predicts that

$$Pe = \frac{4}{C_1 C_2^2}\left[\frac{1 - R_x}{1 + R_x}\right] \quad (11)$$

where C_1 and C_2 are constants and R_x is the correlation coefficient between successive displacements. This coefficient is a measure of the degree of turbulence within a void space. If the flow is streamline, there will be very little mixing and R_x will approach –1, and Pe infinity. If instead mixing is complete within the void, R_x will be zero and the Peclet number constant. The increase in Peclet number with radial position can therefore be attributed to a change in the correlation coefficient from a value near zero at the center of the bed to negative values as the wall is approached. This decrease in correlation coefficient is brought about mainly by an increase in the probability of a deflection toward the direction of an increasing void space and increasing velocity. Both these quantities have been found experimentally to increase as the radial position increases; however there is some uncertainty in using Latinen's expression here since it is based upon the Einstein equation, which itself is dependent upon the assumption that the correlation coefficient is zero (complete mixing).

Qualitative interpretation of the results in terms of the Prandtl mixing-length concept is also of interest. It can be postulated that in the central core of the bed the scale of turbulence is proportional to the particle size and the mean-square deviating velocity is proportional to the superficial velocity in the direction of flow. If the eddy diffusivity is the product of a mixing length (scale of turbulence) and deviating velocity, it is evident that the Peclet number will be constant. As the wall of the pipe is approached, the void fraction increases and it is reasonable to assume that the scale of turbulence also increases. It follows that the decrease in diffusivity, observed as the radial position increases, corresponds to a large decrease in deviating velocity. This conclusion is consistent with the concept that empty pipe behavior is approached near the wall of a packed bed, for in empty pipes the intensity of turbulence, or deviating velocity, is much less than in packed beds. Thus Bernard and Wilhelm (3) have estimated that the intensity is about 40% in fully developed turbulence in packed beds, while the corresponding value in empty pipes is of the order of 2.5 to 5%.

SUMMARY

1. Measured point values of the Peclet number in packed beds increase with radial position. This increase depends upon the particle and pipe size and is significant when D_p/D_t is greater than 0.05.

2. Above modified Reynolds numbers of 40 to 100, the Peclet number is independent of superficial velocity in the pipe and at the center of the bed has a constant value of about 8.0.

3. The change in Peclet number with radial position is due to the increase in void fraction and to the influence of the pipe wall. At up to 81% of the radius the Peclet number could be correlated in terms of void fraction alone, independent of particle size, tube size, and radial position.

4. From a theoretical point of view the increase in Peclet number can be qualitatively explained on the basis of a decreasing intensity of turbulence as the void fraction increases and the pipe wall is approached.

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Hiroo Kurihara assisted in the experimental phase of the project. Professors S. H. Gould, A. J. Perlis, and I. W. Burr of Purdue University gave freely of their counsel in the mathematical and statistical problems. The work was carried out with the financial assistance of the Purdue Research Foundation.

NOTATION

A = constant in series solution of differential equation
C = concentration at a point in the bed, lb./cu.ft.
C_A = measured average effluent concentration, lb./cu.ft.
C_t = concentration of pure carbon dioxide in injection tube
D_p = particle size
D_t = pipe size
E = total effective diffusivity, based upon total area including packing and including the molecular-diffusion contribution
F = function of D_p/D_t used to correlate Pe
G = superficial mass velocity, lb./(hr.) (sq.ft.)
m = function of D_p/D_t used to correlate Pe
Pe = Peclet number, $D_p u/E$
Pe_o = Peclet number at center of bed
r = distance from center of bed
r_o = radius of pipe
R = eigen function
R_x = correlation coefficient between successive displacements
Re = modified Reynolds number, $D_p G/\mu$
t = radial position of radius of injection tube; i.e., radius of injection tube = tr_o
u = superficial velocity at a point in the bed
V = average effluent velocity (superficial)
Y = reading on Micromax recorder for concentration
z = height of packed bed above tip of injection tube

Greek Symbols

δ = void fraction
λ = eigen value
θ = radial position, r/r_o
μ = viscosity of gas flowing through bed

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