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Liquid-phase mass transfer at low flow rates in a packed column

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Liquid-phase mass transfer at low flow rates in a packed column

Abstract
Liquid-phase mass transfer in a packed bed was investigated for flow conditions for which the effect of neglecting axial transfer in the prediction of concentration distributions would most likely be significant. The purpose of this study was twofold: 1) to obtain experimental concentration data suitable for comparison with future theoretical studies, and 2) to analyze these data in terms of calculated effective axial and radial diffusivities and Peclet numbers.

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LIQUID-PHASE MASS TRANSFER AT LOW FLOW RATES IN A PACKED COLUMN

by

John Earnest Frandolig and R. W. Fahien

AMES LABORATORY

RESEARCH AND DEVELOPMENT REPORT

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UNIVERSAL STATES ATOMIC ENERGY COMMISSION

Research and Development Report

LIQUID-PHASE MASS TRANSFER AT LOW FLOW RATES IN A PACKED COLUMN

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John Earnest Frandolig and R. W. Fahien

February, 1964

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LIQUID-PHASE MASS TRANSFER AT LOW FLOW RATES IN A PACKED COLUMN

John Earnest Frandolig and R. W. Fahien

ABSTRACT

Liquid-phase mass transfer in a packed bed was investigated for flow conditions for which the effect of neglecting axial transfer in the prediction of concentration distributions would most likely be significant. The purpose of this study was twofold: 1) to obtain experimental concentration data suitable for comparison with future theoretical studies, and 2) to analyze these data in terms of calculated effective axial and radial diffusivities and Peclet numbers.

The experimental work consisted of measuring radial concentration distributions for a dye being transported in a main stream of water flowing through a 3.97-inch i.d. column packed with 0.262-inch spherical particles. Data were obtained at four axial levels above a centrally located injection tube for Reynolds numbers between 7.1 and 84.9. Samples were removed from the column by a specially designed probe assembly which "averaged" the samples for a given radial position over a number of angular positions.

Analysis of the data was made in accordance with a solution of the boundary value problem set up to describe the physical system. The solution considered the variation of the diffusivities and the flow distribution with radial position. Axial and radial Peclet numbers were calculated for the first time from the data of a single experiment.

Values of the axial Peclet number were found to be approximately one-hundredth of those of the radial Peclet number. Hence, the axial diffusivity is approximately one hundred times greater than the radial diffusivity for the conditions of this study. Although the axial diffusivity was found to be much larger than the radial diffusivity, the effect of including axial transfer in the prediction of concentration distributions was shown to be quite small.

The variation of the radial diffusivity with radial position was found to be much less pronounced than for gas-flow systems as determined by previous investigators.

* This report is based on a Ph. D. thesis submitted by John Earnest Frandolig February, 1964, to Iowa State University, Ames, Iowa.
INTRODUCTION

The successful application of any engineering design technique depends not only on its scientific soundness but also on the quality of the available quantitative descriptions of the various component mechanisms making up the total process. Probably the least understood mechanisms, and certainly very key ones in process design work, are those associated with heat, mass, and momentum transfer in fixed-bed systems. In view of the population density of fixed-bed processes in the chemical and allied industries (e.g., absorption and adsorption processes, fixed-bed catalytic reactors, packed-column distillation and extraction systems, and chromatographic columns), it follows that much attention should be focused on the fundamental aspects of these transfer mechanisms. Present analogies, although incomplete, and possible future ones between the heat, mass, and momentum transfer processes make the study of any one essentially a study of related aspects of the other two.

Mass transport phenomena in cylindrical fixed-bed systems have been studied primarily from two points of view. The first and most generally accepted attack has been that of mathematically characterizing the system by the conventional overall mass transfer coefficient. This type of analysis has been applied to two-phase unit operations such as liquid-liquid extraction and gas-liquid absorption. The results of
these studies are generally applicable only to other identical systems; i.e., systems in which the chemical components, the packing characteristics, and the flow rates are the same. Furthermore, the correlation of dimensionless groups arising from these studies has not been completely successful.

A second approach to the problem is that of considering the mixing, stream-splitting, and molecular diffusion in a binary mixture in a single phase. Studies of this type may be further subdivided into two groups: 1) that in which the total transfer process is characterized by a single effective axial dispersion coefficient (axial dispersivity), and 2) that in which the mass transfer process is characterized by arbitrarily defined coefficients, each of which accounts for the transfer in a given coordinate direction.

The axial dispersivity model has been used to describe unsteady-state and frequency response systems in one spatial dimension. Thus, the axial dispersivity accounts for the mass transfer caused by the combined influence of the velocity profile, molecular diffusion, and the mixing action generated by the presence of the packing. Mathematically, this type of system is described by a material balance around a cylindrical element of the bed which is of differential length $dz$:

$$D_L \frac{\partial^2 C}{\partial z^2} - V \frac{\partial C}{\partial z} = \frac{\partial C}{\partial t}$$

where $C =$ concentration of transferring material

$D_L =$ axial dispersivity
V = mean superficial velocity
z = axial coordinate
\( t = \) time.

Analytical solutions of this equation with various boundary conditions imposed have previously been accomplished (15, 23, 33, 40, 41, 53, 54, 57). Results from this type of analysis are useful in certain simplified reactor designs and in process dynamics studies.

The above two models for describing the mass transfer process in fixed-bed systems have an inherent limitation: the point values of the concentrations are not considered and if the results are to be used for design purposes, point concentrations are not calculable. For a few problems this limitation is not serious. However, in the design of catalytic reactors in which the reaction rate depends on point temperatures and concentrations, these models appear inadequate. The model in which the mass transfer is characterized by directional coefficients allows for the consideration of point concentrations and thus is a more realistic approach to the problem. The detailed mathematical treatment of this model is given in a later section of this report.

In previous fixed-bed studies the axial transfer coefficient, hereinafter referred to as the axial diffusivity, was not evaluated as such. The analysis of experimental concentration data has been restricted by one of two assumptions:
1) the axial diffusivity was assumed equal to the radial diffusivity, or 2) the axial mass transfer was assumed negligible when compared to the bulk flow effect. Results from axial dispersion studies have indicated that both of these assumptions may be invalid, especially in the design of catalytic reactors and extraction systems.

The purpose of this work was twofold: 1) to obtain experimental concentration data suitable for comparison with future theoretical predictions, and 2) to analyze these data in terms of calculated effective axial and radial diffusivities and Peclet numbers. Particular emphasis was placed on determining the effect of neglecting axial transfer on the prediction of concentration profiles for a non-reactive liquid system.

The experimental work consisted of measuring radial concentration distributions for a dye being transported in a mainstream of water flowing slowly through a packed column. The column was 3.97 inches in diameter and was packed with 0.262-inch spherical particles. Data were obtained at four axial levels above a centrally located injection tube for Reynolds numbers between 7.1 and 84.9. Samples were removed from the column by a specially designed probe assembly which "averaged" the sample for a given radial position over a number of angular positions. The data are presented in dimensionless units based on the measured steady-state mean concentration in the column.
Analysis of the data was made in accordance with a solution of the boundary value problem set up to describe the physical system.
Most of the studies of mass transfer in flowing fluids have been carried out primarily in three systems: 1) coaxial fluid streams in ducts, 2) wetted-wall columns, and 3) beds of particles, both fixed and fluidized. The studies involving the coaxial streams may be considered the most basic since, in effect, all processes deal essentially with the flow of fluids in interstices of one kind or another. However, "extrapolation" of new knowledge of this system to the other two is obviously quite dangerous because of the complexity introduced by the two-phases on the one hand, and the particle and packing characteristics on the other. Yet the study of mass transfer in beds of particles has the closest practical chemical engineering application of the three systems as evidenced by the numerous catalytic reactors, absorption columns, chromatographic columns, packed distillation, extraction, and other such towers found throughout the process industries. It is perhaps for this reason that so much basic work has been carried out in this system.

The literature concerning studies of mass, momentum, and heat transfer processes is voluminous. Seagrave (52) presents a quite complete review of mass transfer in coaxial fluid streams in ducts and in wetted-wall columns. Herein is discussed only some of the more pertinent work in the field of
mass transfer as applied to fixed-bed systems. The choice of particular papers covers the many far-ranging aspects of this subject as applied to various unit operations, such as absorption, extraction, and chromatographic separation, and to catalytic reactors.

Flow Distribution

Of prime importance in the study of any fixed-bed transfer process is a knowledge of the distribution of flow across the bed. Primarily because of the increased mathematical complexity of considering a non-uniform flow distribution in fixed-bed calculations, investigators have generally assumed flat profiles in their work. Arthur et al. (4) first showed qualitatively that this assumption is generally invalid. Semi-quantitative results indicated that the flow rate was greatest slightly removed from the containing wall.

Morales et al. (42) and Schwartz and Smith (51), using a hot-wire anemometer, studied this phenomenon at relatively high flow rates for air flowing through beds of cylinders and spheres. They found that the peak velocity occurred approximately one pellet diameter away from the column wall. For the ratio of column diameter to pellet diameter less than 30 this peak velocity ranged from 30 to 100 per cent greater than the velocity at the center of the bed. The divergence of the profile from the assumption of a uniform velocity was found to be
less than 20 per cent only for ratios of column diameter to pellet diameter greater than 30.

The flow distribution may be explained, in part, by the variation of void fraction in the bed. Schaffer (50) and Roblee et al. (48) found that the void fraction in packed cylindrical columns was essentially constant throughout the center of the bed and increased as the wall was approached.

Dorweiler (21), using a hot-wire anemometer, determined the flow distribution for air flowing through a 4.026-inch i.d. column packed with 0.262-inch spherical particles. He concluded that the hot-wire anemometer was sufficiently accurate, on the basis of overall material balances, only for mean superficial velocities above 0.2 foot per second. No data have yet been reported for lower flow rates for either gaseous or liquid systems.

Lapidus (36) carried out time-of-contact (or residence-time) experiments in a packed bed 2.0 inches in diameter with cocurrent flow of liquid and air streams over both porous and nonporous packing. Data for 3.5-millimeter glass beads indicated a close approach to plug flow for the liquid phase. By contrast, residence-time experiments for 1/8-inch porous cylindrical pellets produced distorted curves, the distortion being attributed to mass transfer of tracer from within the internal voids of the packing. When the data of the porous packing were analyzed in terms of combined diffusion and flow
distribution, an effective diffusion coefficient for the inter­ternal pores of the packing could be calculated. The porous packing data, when corrected for this mass transfer effect, then exhibited approximately the same approach to plug flow as those for nonporous packing.

A tracer method was used by Cairns and Prausnitz (14) to determine velocity profiles in packed and fluidized beds. Their results indicated that the profiles for flow through close random packing were essentially flat up to two particle diameters away from the tube wall. Data from the fluidized bed experiments indicated that the flow distribution was a very complex function of particle size, particle density, and tube diameter to particle diameter ratio. In all experiments the tube diameter to particle diameter ratios were equal to or greater than 15.

Mass Transfer

Bernard and Wilhelm (7) were the first to investigate turbulent diffusion in packed beds. A centrally-located tracer injection technique was employed for both liquid and gaseous systems. A solution of the following partial differential equation developed for steady-state diffusion was presented for the assumption that both velocity and diffusivity were constant throughout the bed:
\[
\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial z^2} - \frac{V}{E} \frac{\partial C}{\partial z} = 0
\]

where \( C \) = concentration of diffusing tracer

\( r \) = radial coordinate

\( z \) = axial coordinate

\( V \) = mean superficial velocity

\( E \) = effective diffusivity, assumed to be the same for both the radial and axial directions.

Values of the \( V/E \) ratio and the Peclet number, \( \frac{dpV}{E} \), were calculated using the solution to the differential equation and the experimental concentration data. In the fully developed turbulent region the Peclet number, as a function of the Reynolds number, was correlated by the general expression

\[
Pe = \frac{dpV}{E} = m(Re^1)^n
\]

where \( n \) is a function of the ratio of the particle-to-tube diameters, \( dp/d_0 \), and \( m \) is a function of both \( dp/d_0 \) and packing shape. A difference in the Peclet number of up to 25 per cent between the liquid and gaseous systems was found.

From considerations of the "random walk" theory for fully developed turbulent conditions in a packed bed, Baron (5) predicted a value between 5 and 13 for the Peclet number. Latinen (37) further developed this theory. For a model cubic arrangement of packing, the Peclet number was predicted to be 11.3 for fully developed turbulent conditions.

Ranz (45) developed a method of analysis, based on
properties of a single particle, for estimating and character-
ing transfer rates and pressure drops in packed beds. This
method appears to have application to the design and evalu-
ation of any transfer device which is an assemblage of a large
number of simply shaped interfaces arranged in an ordered or
random pattern. A value of 11.2 for the Peclet number was
predicted for fully developed turbulent conditions in a system
of spherical particles.

Fahien (24) solved the general diffusion equation for
steady-state mass transfer, allowing both the effective radial
diffusivity and the velocity to vary with radial position in
a fixed bed. The solution, considering boundary conditions
of a confining wall and a finite tracer injection tube, was
effected by replacing the differential equation with a set of
homogeneous linear difference equations. Axial diffusion was
assumed negligible when compared to bulk transfer. The effec-
tive radial Peclet number for carbon dioxide in air was found
to vary significantly with radial position, the variation
depending on the ratio of the particle diameter to the column
diameter. An explanation of the variation of Peclet number
with radial position was presented on the basis of an increase
in void fraction with radial position. Average values of the
Peclet number were found to increase with the particle-to-
column diameter ratio and to be substantially independent of
flow rate for Reynolds numbers greater than approximately 150.
Dorweiler (21) extended the data of Fahien (24) for packed beds to very low flow rates. Some interaction of the molecular and eddy mechanisms was illustrated by defining molecular and eddy Peclet numbers and correlating them with Reynolds number.

Plautz and Johnstone (43), applying the technique of Bernard and Wilhelm (7), investigated both heat and mass transfer in a packed bed. Air was used as the main stream fluid, and sulfur dioxide as the tracer gas. Average Peclet numbers were determined for isothermal conditions and for conditions where a radial temperature gradient was impressed. In the fully turbulent region, no effect was obtained; however, at low Reynolds numbers, the Peclet numbers for non-isothermal conditions were less than those for isothermal conditions, the decrease being more pronounced with smaller packing.

Hanratty et al. (27) presented a theoretical analysis of homogeneous isotropic systems involving turbulent mixing. The analysis indicated that the eddy diffusivity becomes constant only for relatively large times of diffusion. Although this analysis was used in conjunction with experimental data from a fluidized system, no characteristic parameter for a fluidized bed was involved. Thus, a similar analysis may be applied to any field of homogeneous isotropic turbulence.

Prausnitz and Wilhelm (44) measured time-average concen-
trations and concentration fluctuations directly above spherical packing in a fixed bed with a small, calibrated, movable electrical conductivity cell. The time-average concentration data were used to calculate values of a Peclet group which appears as a parameter in a theory of concentration fluctuations. The Peclet group had an average value of 10.5 for Reynolds numbers larger than about 200, tube-to-particle diameter ratios larger than about 10, and bed heights larger than about 40 particle diameters.

Klinkenberg et al. (32) presented a mathematical study of steady-state diffusion in a fluid moving in a cylindrical tube at uniform velocity. Axial and radial diffusivities were not assumed to be necessarily equal, but were assumed to be constant throughout the bed. Boundary conditions imposed on the steady-state diffusion equation corresponded to the experimental arrangement of Bernard and Wilhelm (7) in their determination of the eddy diffusion constants.

Hiby and Schümer (29) presented an analysis similar to Klinkenberg et al. (32). An integration of the steady-state diffusion equation, allowing for reflection at the tube wall and for longitudinal diffusion, was given. The solution was evaluated numerically for a range of conditions where longitudinal diffusion was assumed negligible. In formulating the diffusion equation the authors used tensor notation for describing the anisotropic diffusion process.
Roemer et al. (49) calculated diffusion rates for a 2-inch i.d. column packed with 1/8- to 1/2-inch spherical particles and through which nitrogen flowed. Carbon dioxide was injected into the center of the bed and its concentration measured 4.75 inches downstream. Measurements were made for Reynolds numbers between 3 and 80. They found that a point-source solution of the diffusion equation gave values of Peclet numbers about 10 per cent lower than a finite-source solution. The effect of the magnitude of the axial Peclet number on the radial Peclet number was indicated. The final results were obtained by assuming that the axial and radial Peclet numbers were equal.

Beek (6) discusses the utilization of diffusivity results in the design of packed catalytic reactors. He suggests that the radial diffusivity be assumed proportional to the superficial flow distribution. However, Richardson (46) has recently shown that this assumption gives very poor agreement between experimental and calculated mean conversions for the oxidation of sulfur dioxide in a fixed-bed catalytic reactor. He concludes that a variable radial diffusivity calculated using experimental concentration data from a non-reactive system gives significantly better agreement.

A mathematical model for predicting the mixing characteristics of fixed beds of spheres was developed by Deans and Lapidus (18, 19). The model is essentially a two-dimensional
network of perfectly stirred tanks. The predictions of the model were compared with experimentally determined axial and radial mixing parameters by means of the conventional partial differential equation description of flow in fixed beds. Introduction of a capacitance effect was shown to enable the model to predict the abnormally low axial Peclet numbers determined from the data of unsteady state liquid-phase experiments. The application of the model to chemically reactive systems was demonstrated.

Lamb and Wilhelm (34) analyzed the effects of packed bed properties on local concentration and temperature patterns using a "modified stochastic model". Their analysis appears to be the first attempt to develop a stochastic model for fixed-bed equipment.

When a soluble material is injected suddenly into a fluid flowing slowly through a tube, it spreads out along the axial coordinate in both directions by the combined action of molecular diffusion and the variation of velocity over the cross-section. Taylor (57) showed analytically that with certain assumptions the concentration distribution produced is centered on a point which moves with the mean speed of flow and is symmetrical about it in spite of the asymmetry of the flow. Observed concentration distributions were used to calculate a virtual coefficient of "diffusivity" or axial dispersivity. A derived relationship between this dispersiv-
ity and the molecular diffusion coefficient thus provided a new method for determining diffusion coefficients. The coefficient so obtained was found to agree with that determined by other means for potassium permanganate. A later paper described (55) analytically the conditions under which dispersion of a solute in a stream of solvent could be used to determine the molecular diffusion coefficient.

Later, Taylor (56) extended his analysis to include turbulent flow. Experimentally, brine was injected into a straight 3/8-inch pipe and the electrical conductivity was recorded at a point downstream. The theoretical prediction was verified by experiments with both smooth and very rough pipes. An estimate of the effect of the axial diffusion indicated that the correction was very small.

Although Taylor (55, 56, 57) treated experimental data from pipe lines only, his mathematical analyses have no restrictive parameters for such systems and thus may be easily applied to fixed-bed systems.

A new basis for the analysis of dispersion of a solute in a fluid flowing through a tube originally presented by Taylor (55, 56, 57) was developed by Aris (1). This analysis removed the restrictions imposed on some of the parameters at the expense of describing the distribution of solute in terms of its moments in the direction of flow. The general case of diffusion and flow in a straight tube is presented
together with its relation to some special cases.

Converse (16), by a theoretical development similar to that used by Taylor (56, 57) for pipe-line flow, showed the relationship between the effective radial diffusivity, the flow distribution, and the effective axial dispersivity for flow in packed beds. Three calculations were made using a constant effective radial Peclet number of 10. However, the results did not indicate a monotonic trend and are perhaps too limited from which to draw a sound conclusion.

In a reactor the time that the reacting species remain within the system determines the overall conversion. In reality fluid elements of the reactants spend various amounts of time in the reacting zone and thus a distribution of residence times results. Danckwerts (17) showed the effects of longitudinal dispersion on the distribution of residence times for both open and packed tube systems. He further explained how distribution functions for residence times can be defined and measured for actual systems.

Kramers and Alberda (33) treated a sinusoidally varying concentration input to a packed bed from both theoretical and experimental viewpoints. Experimental results for axial dispersion in liquid flow through packed Raschig rings and for back-mixing of a liquid flowing over the packing of an absorption column were compared with the predictions of two mathematical models: 1) the system was treated as a cascade of
perfect mixers, and 2) the response of the system was regarded as the combined result of perfect piston flow and a constant coefficient of axial dispersion. The results were found to deviate significantly from both models. The authors concluded that perhaps such deviation was due, in part, to the non-uniform velocity distribution in the bed. Nevertheless, subsequent investigators have continued to treat the axial dispersion coefficient and the velocity as constants throughout the bed with some degree of success in explaining their experimental results.

Deisler and Wilhelm (20) used a frequency response technique to determine mechanism constants for axial dispersion in the fluid between particles in a bed of porous solids, pore diffusion within the particles, and the composition equilibrium between gases within and outside the particles. Their results indicated that the diffusion constant within the particles was on the order of a few per cent of the normal molecular diffusion constant, but that the axial dispersion between particles for Reynolds numbers between 4 and 50 is significantly larger than for normal molecular diffusion.

A one-dimensional analysis of the boundary conditions for a steady-state flow reactor with axial diffusion, uniform flow distribution, and first order reaction was presented by Wehner and Wilhelm (59). The simultaneous solution of the three differential equations for the reaction, fore, and after
sections led to conclusions regarding reactor properties. Contributions of axial mass transfer in the three parts of the system to the course of the reaction in space were considered.

Levenspiel and Smith (39) presented methods for evaluating the axial dispersion coefficient from experimental measurements. Examples were worked out and conditions for the applicability of the model were discussed. The axial dispersion coefficient was assumed to be independent of position for either of the following two conditions: 1) when the fluid velocity and mixing are uniform, and 2) when the lateral dispersions of material (by either molecular diffusion or turbulent mixing) is great enough to insure a uniform tracer concentration at any given cross section.

Several investigators added to the work of Levenspiel and Smith (39). Van der Laan (58) treated the problem in a more general manner so as to include the case of finite pipe length and that of a varying axial dispersivity. Aris (2) showed that a suitable analysis was possible for tracer injections other than that of the delta function form. Bischoff (8) presented a different procedure for finding first and second moments from which the axial dispersivity could be calculated.

McHenry and Wilhelm (41) studied the axial mixing of binary gas mixtures flowing in a random bed of spheres. The systems \( \text{N}_2-\text{H}_2 \) and \( \text{C}_2\text{H}_4-\text{N}_2 \) were studied for Reynolds numbers
between approximately 100 and 400. For twenty-one determinations the mean effective axial Peclet number was $1.88 \pm 0.15$. This is in excellent agreement with the theoretical value of $2.0$ for the assumption that the bed of particles acts as a series of perfect mixers, the number of mixers being equal to the number of particles traversed between inlet and outlet points in question. Thus the axial dispersivity for turbulent flow of gases among particles appears to be about sixfold larger than the effective radial diffusivity previously determined. This suggests that perhaps axial diffusion effects may not be neglected in contacting devices such as adsorbers and catalytic reactors.

Aris and Amundson (3) compared the solutions obtained from the mixing cell model and a turbulent diffusive mechanism model. They showed that the effective axial Peclet number for agreement of the two must be about two, as a limiting case for high Reynolds numbers. This result was further substantiated by experimental data.

Ebach and White (23) used both a frequency response technique and a pulse function method to investigate the axial mixing of liquids flowing through fixed beds of solids. Variables investigated were fluid velocity, particle diameter, particle shape, and liquid viscosity. Effective axial Peclet numbers varied from 0.3 to 0.8 for the range of Reynolds numbers from 0.01 to 150.
Carberry and Bretton (15), using a pulse input of dye in water, essentially corroborated the results of Ebach and White (23). They also briefly investigated the dispersion of a pulse of air injected into a stream of helium flowing through a gas chromatographic column. For Reynolds numbers less than 1 the axial dispersivity was found to be about equal to the calculated molecular diffusivity of this gas system.

Experimental longitudinal "diffusivity" data for packed beds were obtained by Strang and Geankoplis (54) using a frequency response technique. Aqueous solutions of 2-naphthol were used as tracers in a main water stream passing through a 4.2-centimeter column packed with either 0.60-centimeter glass beads, 0.63-centimeter Alcoa H-151 porous alumina spheres, or 7x7-millimeter Raschig rings. Experiments were conducted over a Reynolds number (based on mean interstitial velocity in the bed) range of 14.1 to 46.9. Values of $D_L$ and $P_e_z$ were determined as a function of Re.

Cairns and Prausnitz (13) investigated longitudinal mixing properties of a water stream flowing through 2-inch and 4-inch tubes each packed with 1.3-, 3.0-, and 3.2-millimeter spheres over the Reynolds number range 3 to 4500. Experiments consisted of injecting a step function of salt solution through a simulated plane source and measuring point concentration breakthrough curves with electrical conductivity probes. The results were reported in terms of an eddy "diffu-
sivity" as a function of hydraulic radius and line velocity which are proposed as the characteristic length and velocity terms. The "diffusivities" are somewhat lower than those of other investigators who used radially integrated rather than point measurements of the breakthrough curve. It was shown that the integrated results are too high because of a non-flat velocity profile.

Cairns and Prausnitz (12) also studied the longitudinal mixing properties in liquid-solid fluidized beds by means of a step function response technique. The data reduction technique yielded non-flat "diffusivity" (actually dispersivity) profiles. The results were consistent with the fact that the fluidized bed may be considered as a transition between a packed bed and an open tube.

Liles and Geankoplis (40) recognized and evaluated end effects and the effect of column length on the axial dispersivity for liquids by frequency response studies. When end effects were eliminated by an experimental technique for the analysis of the inlet and outlet streams, no effects of length on the dispersivity were found. However, when end effects were artificially introduced by using void analytical sections at the two ends, the dispersivity was found to decrease as the length of the bed was increased until a certain point, after which it remained constant with increase in length. The overall results were in general agreement with the data of others (13, 15, 23, 33, 54).
Robinson (47) calculated longitudinal dispersion coefficients for three binary gas systems: helium-air, air-ethylene, and nitrogen-ethylene. Calculations were made using data from experimental measurements of the dispersion of a step function input to columns packed with glass beads. The columns were 3/8-inch tubing packed with 0.0246-inch beads and were 10, 20, and 40 feet in length, respectively. Coefficients were calculated for the Reynolds number range from 0.03 to 1.0.

The effects of axial and radial diffusion on the mass transfer coefficient for air flowing through a bed of naphthalene pellets were evaluated by Bradshaw and Bennett (11). Values of the mass transfer coefficient as a function of radial position were calculated from a differential mass balance for naphthalene by graphical differentiation of the various concentration profiles. Data on the radial variation of the effective radial diffusivity (25), the superficial velocity (51), and the void fraction (48) were used in the final calculations. The axial term, involving a constant axial Peclet number of 2.0, was included in the calculation, but was found to have only minor effect on the final results. The mass transfer coefficient was found to reach a maximum at a dimensionless radial position of approximately 0.7 for Reynolds numbers ranging from 438 to 9900.

Bischoff and Levenspiel (9) summarized the mathematical models used to characterize dispersion of fluids in flowing
systems. The models in which plug flow was assumed were discussed and compared. These models were shown to be special cases of a very generalized model. In a second paper (10) the authors related these plug flow models to the more general models which do not assume plug flow nor constant values for the dispersion coefficients.

Gottschlich (26) showed that the discrepancy between axial dispersivities for gas-flow and liquid-flow experiments may be explained by including the effect of a stagnant film. His analysis indicated that this mixing film has an effect on dispersion only in unsteady-state processes. The quantitative nature of this film is such that it causes the effective axial Peclet number for liquid-flow experiments to be smaller than the theoretical value of 2.0 derived from the mixing cell model. Thus, in steady state processes, such as a typical catalytic reactor, the axial Peclet number should be approximately 2.0, whether for gas- or liquid-flow systems.

Houston (30) proposed a theory of elution chromatography for the design of large-size chromatographic columns. The dispersion of the solute band was attributed to axial dispersion. Associated experimental studies showed the effective axial dispersivity to be dependent on the flow rate and size of the solute sample. The effective axial Peclet number decreased from 0.11 to 0.06 (0.2 < Re' < 1.8) with increasing flow (using benzene) and also decreased from 0.16 to 0.06 when
sample size was varied from 0.6 to 6.3 micromoles of solute (using toluene).

Jacques and Vermeulen (31) studied the dispersion phenomena in packed beds in both the axial and radial directions to provide basic data for extraction tower design. Results were presented as radial and axial Peclet numbers for both one-phase and two-phase flow.

Sleicher (53) theoretically analyzed the effect of back-mixing of either phase in an extraction column, which decreases the extraction efficiency, by means of an idealized diffusion model. Calculations for a wide range of the model parameters, a Peclet number for each phase, a mass transfer number, and the usual extraction factor, were performed on a digital computer. The principal results, presented in tabular form, should be useful in the design and scale-up of extraction columns and in the interpretation of experimental results from extractors and from some reactors in which a first-order reaction occurs.

Hennico et al. (28) determined axial dispersion coefficients for both the continuous and dispersed phases for the two-phase countercurrent flow of water and kerosene in packed columns. Their results indicated that longitudinal dispersion is an important effect and should be calculated as an independent factor in extraction column design.

Levenspiel and Bischoff (38) summarize the important
results from axial dispersion studies. They discuss the utility of the axial dispersion model in the design of specific fixed-bed systems.
EQUIPMENT AND PROCEDURE

The experimental apparatus used in this study is shown schematically in Figure 1. The equipment may be divided functionally into a water filtering and metering section, a tracer material metering section, a test column, a sampling section, and an analytical instrument.

Water from the building supply was used as the bulk stream liquid. Scale and dirt particles were removed from the water stream by a 10-micron Cuno Micro-Kleen filter. It was further necessary to remove dissolved air from the water supply since it caused bumping and generally unstable conditions in the test column. This was accomplished by passing the water into the top of a 10-foot high, 4-inch diameter combination surge, constant-head, and overflow tank. As the water flowed down this column, the air had a tendency to escape upward to the lower pressure area and consequently passed out the overflow line. After the water passed from the bottom of the surge tank, it was metered by a 600-millimeter Brooks rotameter capable of measuring flow rates of 0.1 to 2.0 gallons per minute. The flow rate was controlled by two globe valves: a 3/4-inch valve preceding the filter and a 1/2-inch valve preceding the rotameter.

A 2.0 gram per liter water solution of fluorescein disodium salt (dye) was used as the tracer material. The dye was fed from a 4-liter storage tank pressurized by nitrogen.
Figure 1. Flow and sampling diagram
A two-stage pressure regulator was used to insure a constant pressure on the storage tank. The dye flow rate was controlled by a 1/8-inch precision needle valve in conjunction with a model 63BD-L Moore constant differential type flow controller. The rate was measured by a 150-millimeter Brooks rotameter with a flow rate range of 1.0 to 16.0 milliliters per minute.

The test column consisted of a vertical 32-inch copper pipe to which could be attached various lengths of transparent acrylic tube. The average inside diameter was 3.97 inches. A packing support, consisting of 0.045-inch stainless steel wire screen with 0.2-inch square openings set on top of a reinforced stainless steel circular frame, was held in position 13 inches above the base plate of the column by three 3/16-inch bolts.

A 0.186-inch i.d. stainless steel tracer injection tube entered the column at a point 3.5 inches above the base plate. It was centrally located and held in place by the packing support frame and its own rigid fastening through the wall of the column. The injector extended to a point 8.0 inches from the top of the copper pipe. When packing the column to the level of the tip of the injection tube, a spoke-wheeled device was slipped over the tube to hold it rigidly in place. The column was packed using a slow, rotary pouring motion.

The packing was 1/4-inch nonporous, ceramic, spherical
pellets (21). Because of the irregularity of the particles, an effective diameter was determined by measuring the volume of water displaced by 1300 pellets and calculating the diameter equivalent to this number of perfect spheres. The diameter thus determined was 0.262 inches.

The height of the packed bed above the injection tube was varied by screwing additional lengths of the acrylic tube to the base section. The connections were such that overlapping grooves formed smooth inner seals.

When the column had been packed to the desired height above the injection tube, one of two sampling assemblies was attached. Figure 2 depicts the multiple probe assembly in position on top of the test column. This device was constructed such that at each radial position a number of equiangular probes entered a common outlet line downstream from the top of the packing. The individual probes were 1/8-inch i.d. and 3/16-inch o.d. The first radial position had four individual probes 90 degrees apart. These were attached to a common outlet which protruded through the column wall. On the outside of the column a stopcock to control the sampling rate was attached. Probes were located at six other radial positions. Table 1 summarizes the probe positions.

The individual probes were located in their respective radial positions to within a tolerance of ± 0.005 r units by using the plate shown in Figure 4. This plate was used...
Figure 2. Experimental equipment with multiple probe assembly attached

Figure 3. Experimental equipment with single probe assembly attached
Table 1. Multiple probe assembly data

<table>
<thead>
<tr>
<th>Radial position, r*</th>
<th>Number of individual probes</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.173</td>
<td>4</td>
</tr>
<tr>
<td>0.316</td>
<td>4</td>
</tr>
<tr>
<td>0.447</td>
<td>4</td>
</tr>
<tr>
<td>0.548</td>
<td>6</td>
</tr>
<tr>
<td>0.707</td>
<td>6</td>
</tr>
<tr>
<td>0.837</td>
<td>8</td>
</tr>
<tr>
<td>0.949</td>
<td>12</td>
</tr>
</tbody>
</table>

not only to locate the probes before rigidly fastening them in place but also to frequently check their positions.

Because of space limitations no suitable center line probe could be placed in the multiple probe assembly. Thus, in order to remove a sample from the center of the column, the multiple probe was replaced by a single probe assembly. Figure 3 shows the single probe in position on top of the test column. This sampling device consisted of a 1/4-inch i.d. thin-walled pitot probe housed in a 6-inch section of acrylic tube. This sampler was constructed such that a sample could be withdrawn from any radial position in the bed. However, for this study it was used only to remove a center line sample.

A 12-inch discharge section was attached to the single probe assembly to help prevent convection currents from disturbing the flow emerging from the top of the packing. Thus,
Figure 4. Multiple probe positioning plate
the column extended a total of 18 inches above the packing. For the multiple probe assembly the same result was achieved by making the housing 18 inches in length.

The temperature of the effluent stream was measured by a thermometer located at the top of the column. This temperature was taken as the characteristic temperature of the system and was also used to indicate the system's approach to equilibrium.

The effluent from the column passed into an overhead tank: the 5-gallon can shown at the top of Figures 2 and 3. The stream entered the side of the tank, "splashed" into the bottom, and flowed by gravity down a drain line to the sewer. This tank served three purposes: 1) it aided in mixing the effluent stream from which a sample was needed to reduce the concentration distributions to $C/C_E$ units; 2) it allowed discharge of the effluent without influencing the test section; and 3) it provided a constant head for forcing the samples through the probes.

A sampling valve was located immediately preceding the point at which the effluent stream entered the sewer. The concentration of the sample removed here was the steady-state mean concentration in the column, $C_E$.

The concentration of the samples were determined with a precalibrated Bausch and Lomb Spectronic 20 colorimeter operated at a wavelength of 4900 angstroms. At this wave-
length the instrument had a range of 0.00 to 6.00 milligrams dye per liter. Since some samples were of higher concentration, it was necessary to dilute them before measurement and then to calculate the concentration of the original samples.

The experimental procedure was quite simple. The test column was first packed to the desired height above the injection tube. One of the two sampling assemblies was then attached. The flow rates of the dye and water streams were set to the desired values. The dye rate was fixed such that the mean injection velocity was approximately equal to the main stream superficial velocity. Depending on the flow rate a period of 30 to 90 minutes was allowed for the system to reach equilibrium. The criteria for equilibrium were that the flow rates remained constant for approximately 30 minutes and that thermal equilibrium was reached as indicated by the temperature of the effluent stream. When using the multiple probe sampler, samples were removed from all the radial positions simultaneously. The sampling rates were set such that the mean linear velocity in each probe was approximately equal to the mean superficial velocity in the column. Accounting for the lag time appropriate to the flow rate a "cup-mixed" sample was taken from the effluent stream. This sample corresponded to the mean concentration in the column at the time the radial samples were collected.

The above procedure was repeated for each desired flow
rate. Experiments were performed for three to five flow rates after which the samples were analyzed with the colorimeter.

When the desired experiments were completed with the multiple probe, the single probe was used to establish the center concentrations for the particular height of packing. Then the packing height was changed and the entire process was repeated.
MATHEMATICAL ANALYSIS

Development of the Boundary Value Problem

The total rate of a material transferred by the combined processes of molecular and turbulent diffusion in a fluid flowing in a duct has been mathematically expressed (52) by

\[ \mathbf{J} = - (D \mathbf{I} + E_t) \cdot \nabla \mathbf{C} = - E \cdot \nabla \mathbf{C} \] (4)

where \( \mathbf{J} \) = mass transfer flux vector
\( \mathbf{C} \) = concentration of transferring material
\( \nabla \) = gradient operator
\( D \) = molecular diffusion coefficient
\( \mathbf{I} \) = unit second-order tensor

\[ \mathbf{I} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \]

\( E_t \) = turbulent diffusivity tensor

\[ E_t = \begin{pmatrix} E_{trr} & E_{t\phi r} & E_{t\phi z} \\ E_{t\phi r} & E_{t\phi \phi} & E_{t\phi z} \\ E_{t\phi z} & E_{tz\phi} & E_{tzz} \end{pmatrix} \]

in cylindrical coordinates \((r,\phi,z)\)

\( E \) = total diffusivity tensor

\[ E = \begin{pmatrix} E_{rr} & E_{r\phi} & E_{rz} \\ E_{\phi r} & E_{\phi \phi} & E_{\phi z} \\ E_{zr} & E_{z\phi} & E_{zz} \end{pmatrix} \]

Equation 4 expresses the molecular and turbulent processes as though they occur in parallel. For flow in an
unpacked tube this may be partially correct, although the turbulent transport process is itself nevertheless influenced by molecular diffusion. However, in any case, it must be recognized that Equation 4 is an arbitrary definition of $E$, which is only an empirical coefficient.

If one accepts the general differential equation description of fixed-bed processes (i.e., one assumes a smooth variation of properties on a macroscopic scale), a description of the mass transfer process taking place in the fluid moving in the interstices of the packing may be written

$$J = -E \cdot \nabla C$$

(5)

where the separation of the molecular and turbulent processes is not indicated. It is felt that no distinct separation of the two processes can be made for a fixed-bed system. The diffusivity for the packed bed defined by Equation 5 must not be confused with that of the unpacked tube defined by Equation 4. Each must be determined by the analysis of experimental data from its respective physical configuration. Unless otherwise stated, the term "diffusivity" as used in this work will be that associated with a packed bed. Undoubtedly the components of the diffusivity tensor are very complicated functions of the column diameter, packing characteristics, flow rate, and perhaps fluid properties (especially at low flow rates).

Using the above nomenclature the general equation for
mass transfer of a given species in a binary fluid in a packed bed may be written

$$\frac{\partial C}{\partial t} = - \nabla \cdot (- E \cdot \nabla C) - \nabla \cdot (C \mathbf{u})$$  \hspace{1cm} (6)

where \( \mathbf{u} \) = superficial velocity vector
\( t = \) time.

Although the present study involves a system most easily described by cylindrical coordinates, Equation 6 holds irrespective of the coordinate system used. Thus, the components of \( E \) determined in one coordinate system may be modified by a simple transformation for use in a second system. As a point of warning, however, the values of the individual elements as determined for one geometrical configuration do not generally apply to a second physical system.

For the purposes of this study several assumptions are made concerning the terms in Equation 6. They may be summarized as follows:

1. The non-diagonal elements of \( E \) have been assigned a value of zero. Thus, net mass transfer in any coordinate direction is said to occur only if there exists a concentration gradient in that direction.

2. The fluid is incompressible \( (\nabla \cdot \mathbf{u} = 0)\).

3. The system has reached the steady-state condition; i.e., all variables are independent of time.

4. The system is angularly symmetric. Microscopically, this is not true, but on a macroscopic scale it is an accept-
40

able assumption.

5. The system is macroscopically homogeneous in the
direction of net flow.

6. The radial diffusivity, $E_r$, hereinafter denoted by
$E_r$ and the axial diffusivity, $E_z$, hereinafter denoted by $E_z$,
are functions of radial position only.

7. Net flow is in the axial direction only and the
flow distribution is a function of radial position only.
Under these assumptions Equation 6, expressed in cylindrical
coordinates, becomes

$$
\frac{1}{r} \frac{\partial}{\partial r} \left( r E_r(r) \frac{\partial C}{\partial r} \right) + E_z(r) \frac{\partial^2 C}{\partial z^2} = u_z(r) \frac{\partial C}{\partial z}.
$$

(7)

For calculational purposes it is convenient to write
Equation 7 in dimensionless form. The following dimensionless
variables are used:

$$
r^* = \frac{r}{r_0}
$$

$$
r^*_p = \frac{r_p}{r_0}
$$

$$
z^* = \frac{z}{r_0}
$$

$$
d^*_p = \frac{d_p}{r_0}
$$

$$
v^* = \frac{u_z(r)}{V}
$$

$$
v^*(r^*_p) = \frac{u_z(r_p)}{V}
$$

$$
c^* = \frac{C}{C_E}
$$

$$
p = \frac{E_r(r)}{E_r(r_p)}
$$

$$
pe_r(r^*_p) = d_p \cdot \frac{u_z(r_p)}{E_r(r_p)}
$$

$$
pe_z = d_p \cdot \frac{u_z(r)}{E_z(r)}
$$

(8)
where \( r_0 \) = column radius

\( r_p \) = a specified radial position

\( d_p \) = mean packing diameter

\( V \) = mean superficial velocity

\( C_E \) = measured effluent concentration.

Equation 7 then becomes

\[
\frac{1}{v*r^*} \frac{\partial}{\partial r^*} \left( r^* p \frac{\partial C^*}{\partial r^*} \right) + \frac{Pe(r^*_p)}{Pe_v(r^*_p)} \frac{\partial^2 C^*}{\partial z^*} = \frac{Pe(r^*_p)}{\bar{d}^*_p v^*(r^*_p)} \frac{\partial C^*}{\partial z^*} .
\]

Equation (9)

The boundary value problem is completed by specifying conditions which describe the experimental system. These are:

I. At the arbitrarily chosen zero bed height, the plane of the tip of the injection tube, the concentration over the face of the tube is constant at \( C_1^* \); and outside the tube it is zero:

\[
C^*(r^*,0) = C_1^* \quad 0 \leq r^* \leq r_1^* \\
= 0 \quad r_1^* < r^* \leq 1.0 .
\]

II. As the height above the injection tube becomes great, the concentration at any radial position approaches the mean integral concentration:

\[
\lim_{z^* \to \infty} C^*(r^*,z^*) = C_0^* .
\]

III. The concentration gradient is bounded:

\[
\frac{\partial C^*}{\partial r^*} (0,z^*) = 0 .
\]
IV. No net mass transfer occurs at the wall:

\[ \frac{\partial C^*}{\partial r} (1.0, z^*) = 0 . \]

Solution of the Problem

The method of solution of Equation 9 with its associated boundary conditions is patterned after that of Fahien (24). The only difference is that herein the axial mass transfer is not neglected. However, it is necessary to assume that the axial Peclet number is constant. This assumption will be discussed later.

A particular solution of the form

\[ C^*(r^*, z^*) = R(r^*) \cdot Z(z^*) \]  \hspace{1cm} (10)

is postulated and substituted into Equation 9, resulting in the following separation of variables:

\[ \frac{1}{v^* r^* R} \frac{d}{dr^*} \left( pr^* \frac{dR}{dr^*} \right) = \frac{Pe_r(r^*)}{d^* v^*(r^*) Z} \frac{dZ}{dz^*} - \frac{Pe_r(r^*)}{Pe_z v^*(r^*) Z} \frac{d^2Z}{dz^* Z} = - \beta \] \hspace{1cm} (11)

where \( \beta \) is a real positive number. Thus Equation 11 may be written as two ordinary differential equations:

\[ \frac{d^2Z}{dz^* Z} - \frac{Pe_z}{dp^*} \frac{dZ}{dz^*} - \frac{\beta Pe_z v^*(r^*)}{Pe_r(r^*)} Z = 0 \] \hspace{1cm} (12)

and

\[ \frac{d}{dr^*} \left( pr^* \frac{dR}{dr^*} \right) + \beta v^* r^* R = 0 . \] \hspace{1cm} (13)

The solution of Equation 12 is
\[ Z = \exp \left[ \left( 1 - \sqrt{1 + \frac{4d_P^* v^*(r_P^*)}{Pe_z Pe_r(r_P^*)} \frac{Pe_z z^*}{2d_P^*}} \right) \right] \]  

(14)

where boundary condition II has been imposed. The constant coefficient is omitted here since \( Z \) is later used in a product containing another constant.

Equation 13 together with boundary conditions III and IV constitute a Sturm-Liouville problem. For each eigen value \( \beta_n \) there is a solution \( R_n \) not identically zero. Any two of these solutions are orthogonal on the interval \( 0 \leq r^* \leq 1.0 \) with respect to the weight function \( v^* \cdot r^* \). This problem has been solved numerically (24). The use of a numerical approach allows \( p \) and \( v^* \) to be quite arbitrary. It is only necessary here to assume that they are known functions, at least in tabular form.

Consider the equally spaced points, \( k = 0, 1, 2, \ldots, N \), in the interval \( 0 \leq r^* \leq 1.0 \). If Equation 13 is written in central difference form for the general point \( k \) and then rearranged, the result is

\[
\left[ p(k - \frac{1}{2}) \cdot r^*(k - \frac{1}{2}) \right] \cdot R(k - 1) \\
\left[ \beta \cdot h^2 \cdot v^*(k) \cdot r^*(k) - p(k + \frac{1}{2}) \cdot v^*(k + \frac{1}{2}) - \\
p(k - \frac{1}{2}) \cdot r^*(k - \frac{1}{2}) \right] \cdot R(k) + \\
\left[ p(k + \frac{1}{2}) \cdot r^*(k + \frac{1}{2}) \right] \cdot R(k + 1) = 0
\]  

(15)

where \( h \) is the interval between two adjacent points.
Equation 15 is valid for any point except at the column center (\( k = 0 \)) and at the column wall (\( k = N \)). The equation for the column center is obtained by expanding Equation 13, introducing boundary condition III, and using a meaningful value of the weight function \( v^* \cdot r^* \). The result is

\[
\left[ \frac{1}{4} \cdot \beta \cdot h^2 \cdot v^*(\frac{1}{2}) \cdot r^*(\frac{1}{2}) - p(\frac{1}{2}) \cdot r^*(\frac{1}{2}) \right] \cdot R(0) + \left[ p(\frac{1}{2}) \cdot r^*(\frac{1}{2}) \right] \cdot R(1) = 0
\]

where

\[
v^*(0) \cdot r^*(0) = \frac{1}{4} \cdot v^*(\frac{1}{2}) \cdot r^*(\frac{1}{2}) .
\]

Similarly for the column wall,

\[
\left[ p(N - \frac{1}{2}) \cdot r^*(N - \frac{1}{2}) \right] \cdot R(N - 1) + \left[ \frac{1}{4} \cdot \beta \cdot h^2 \cdot v^*(N - \frac{1}{2}) \cdot r^*(N - \frac{1}{2}) - p(N - \frac{1}{2}) \cdot r^*(N - \frac{1}{2}) \right] \cdot R(N) = 0
\]

where boundary condition IV has been imposed. The meaningful weight function used at the wall is

\[
v^*(N) \cdot r^*(N) \equiv \frac{1}{4} \cdot v^*(N - \frac{1}{2}) \cdot r^*(N - \frac{1}{2}) .
\]

The equations representing the \( N - 1 \) internal points, the point at the center, and the point at the wall form a system of \( N + 1 \) simultaneous homogeneous linear equations. These equations may be written in matrix form:

\[
(\beta D(k) - B1(k)) \cdot R(k) = 0
\]
or

\[(A(k) - \beta I) \cdot R(k) = 0 \quad (21)\]

where \(A(k) = D^{-1}(k) \cdot B_1(k)\)

\(I = \text{unit matrix.}\)

By setting the determinant of \((A(k) - \beta I)\) equal to zero, the roots of the resulting polynomial may be calculated. These roots are the eigen values \(\beta_n\) of the system. Once an eigen value has been found, the associated eigen function \(R_n(k)\) may be evaluated by solving the system of equations represented by Equation 21. Since \(A(k)\) is a real symmetric matrix, it follows that the eigen functions are orthogonal to each other.

The methods used to calculate the eigen values and eigen functions are presented by Lapidus (35) in the form of equations which are ideally suited for digital computations. Details of the calculations are given in Appendix B in the form of a FULL FORTRAN program written for an IBM 7074 digital computer.

Inspection of the defining polynomial \(|A(k) - \beta I| = 0\) indicates that \(\beta_0 = 0\). Further, the eigen functions as defined by Equation 21 are calculable only in terms of an arbitrary constant, say \(R_n(0)\). Since \(R_n(k)\) is used only in a product containing an arbitrary constant, it is convenient to set \(R_n(0)\) equal to unity. Thus from Equations 15, 16, and 18, it is easily seen that \(R_0(k) = 1.0\) for all \(k\).

The complete solution of Equation 9 with its associated boundary conditions is a linear combination of the particular solutions and is given by
\[ C^*(k, z^*) = \sum_{n=0}^{N} A_n^1 \cdot R_n(k) \cdot Z_n(z^*) \quad (22) \]

where \( n \) designates the set of solutions to Equation 21 and \( k \) the radial position. The constants \( A_n^1 \) are determined from consideration of boundary condition I and the orthogonality of the eigen functions.

Multiplying Equation 22 by \( R_m \cdot v^*(k) \cdot r^*(k) \cdot h \) and summing on \( k \) at \( z = 0 \) gives

\[ \left[ r_1^* \right] = \sum_{k=0}^{l} R_n(k) \cdot v^*(k) \cdot r^*(k) \cdot C_1^* = \]

\[ \sum_{k=0}^{N} A_n^1 \cdot R^2_n(k) \cdot v^*(k) \cdot r^*(k) \quad (23) \]

since

\[ \sum_{k=0}^{N} R_m(k) \cdot R_n(k) \cdot v^*(k) \cdot r^*(k) \neq 0 \quad n = m \quad (24) \]

\[ = 0 \quad n \neq m \]

by orthogonality of the eigen functions. Rearranging,

\[ A_n^1 = \frac{\left[ r_1^* \right] + 1}{\sum_{k=0}^{N} R^2_n(k) \cdot v^*(k) \cdot r^*(k)} . \quad (25) \]

In the expansion of the numerator \( r_1^* \) will generally correspond to a radial position somewhere in the range \( 0 \leq k \leq l \). Thus linear interpolation is used:
\[
\sum_{k=0}^{[r_1^*] + 1} R_n(k) \cdot v^*(k) \cdot r^*(k) = 
R_n(0) \cdot \frac{1}{4} \cdot v^*(\frac{1}{2}) \cdot r^*(\frac{1}{2}) + \frac{r_1^*}{h} \cdot R_n(1) \cdot v^*(1) \cdot r^*(1).
\]

(26)

Summations are employed rather than integrations since the eigen functions are defined only at the mesh points \( k \).

A mass balance over the cross section at any column height yields the integral mean concentration:

\[
C^*_M = \frac{\sum_{k=0}^{[r_1^*] + 1} v^*(k) \cdot r^*(k)}{\sum_{k=0}^N v^*(k) \cdot r^*(k)} = \frac{\sum_{k=0}^N C^*(k, z^*) \cdot v^*(k) \cdot r^*(k)}{\sum_{k=0}^N v^*(k) \cdot r^*(k)}.
\]

(27)

Substituting into Equation 25 gives

\[
A_n' = C^*_M \cdot \frac{\sum_{k=0}^N v^*(k) \cdot r^*(k)}{\sum_{k=0}^{[r_1^*] + 1} v^*(k) \cdot r^*(k)} = \frac{\sum_{k=0}^{[r_1^*] + 1} R_n(k) \cdot v^*(k) \cdot r^*(k)}{\sum_{k=0}^N R_n^2(k) \cdot v^*(k) \cdot r^*(k)}.
\]

(28)

Since \( R_0(k) = 1.0 \) for all \( k \),

\[
A_0' = C^*_M
\]

and thus Equation 22 may be written

\[
C^*(k, z^*) = C^*_M + \sum_{n=1}^N A_n' \cdot R_n(k) \cdot z_n(z^*).
\]

(30)

In order to use one set of eigen values and eigen
functions for computer calculations involving more than one set of concentration data, new constants may be defined such that

\[ B_n = \frac{A_n}{C_M^*}. \]  

Equation 30 then becomes

\[ C^*(k,z^*) = C_M^*(1 + \sum_{n=1}^{N} B_n \cdot R_n(k) \cdot Z_n(z^*)). \]  

The procedure for calculating the constants \( B_n \) is an integral part of the computer program given in Appendix B.

Treatment of Experimental Data

The above solution implies that if one knows \( p, v^*, Pe_z, \) and \( Pe_r(r_p^*) \), the concentration may be calculated for the general point \((k,z^*)\). However, the problem at hand is somewhat different. It may be stated as follows: Given an experimentally determined flow distribution \( v^* \) and sufficient concentration data \( C^* \), find values of the radial Peclet number \( Pe_r(r_p^*) \) and the axial Peclet number \( Pe_z \), and determine the radial variation of the radial diffusivity \( Er \) (i.e., find how \( p \) varies with \( r^* \)). Consider first the function \( p \).

Determination of the radial variation of \( p \)

Since \( B_n \) becomes increasingly larger with \( n \), it follows that \( Z_n \) becomes progressively smaller. In turn the successive terms in Equation 30 decrease in size very rapidly. Thus for
very large values of $z^*$ the finite series in Equation 30 may
be quite accurately approximated by the first two terms only:

$$C^*(k,z_1^*) = C_M^* + A_1^* \cdot R_1(k) \cdot Z_1(z_1^*)$$

(33)

where $z_1^*$ represents some arbitrarily large axial distance from
the injection tube. Solving for $R_1(k)$ gives

$$R_1(k) = \frac{C^*(k,z_1^*) - C_M^*}{A_1^* \cdot Z_1(z_1^*)}.$$  

(34)

Consider the tube center difference equation, Equation
16, for the case of the first non-zero eigen value $\beta_1$ and its
 corresponding eigen function $R_1(k)$. Solving for $p(\frac{1}{2})$ and
substituting Equation 34 evaluated for the respective cases
$k = 0$ and $k = 1$ results in

$$p(\frac{1}{2}) = \frac{1}{4} \cdot \beta_1 \cdot h^2 \cdot v^*(\frac{1}{2}) \cdot (C^*(0,z_1^*) - C_M^*)}{C^*(0,z_1^*) - C^*(1,z_1^*)}.$$  

(35)

If the same procedure is applied to the general equation,
Equation 15, for $k = 1$, and $p(\frac{1}{2})$ from above is substituted,
the result is

$$p(\frac{3}{2}) =$$

$$\beta_1 \cdot h^2 \cdot \left[ \frac{1}{4} \cdot v^*(\frac{1}{2}) \cdot r^*(\frac{1}{2}) \cdot (C^*(0,z_1^*) - C_M^*) + v^*(1) \cdot r^*(1) \cdot (C^*(1,z_1^*) - C_M^*) \right]$$

$$r^*(\frac{3}{2}) \cdot (C^*(1,z_1^*) - C^*(2,z_1^*))$$

(36)

Continuation of this process results in the general form:
Recalling the defining expression for the function \( p \),
\[
    p = \frac{E_r(r) / E_r(r_p)}{r^*(k + \frac{1}{2}) \cdot (C^*(k, z_1^*) - C^*(k + 1, z_1^*))},
\]
(37)

it is now convenient to fix \( r_p^* \), and thus \( r_p \), such that
\[
    r_p^* = r^*(k + \frac{1}{2}) = r^*(\frac{1}{2}) = h/2 .
\]
(39)

Then
\[
    p(r_p^*) = p(\frac{1}{2}) = 1.0
\]
(40)

and Equation 35 may be rearranged to give
\[
    \beta_1 \cdot h^2 = \frac{(C^*(0, z_1^*) - C^*(1, z_1^*))}{\frac{1}{4} \cdot v^*(\frac{1}{2}) \cdot (C^*(0, z_1^*) - C_M^*)}
\]
(41)

Substituting into Equation 37 gives
\[
    p(k + \frac{1}{2}) = \frac{(C^*(0, z_1^*) - C^*(1, z_1^*) \cdot \sum_{k=0}^{k} v^*(k) \cdot r^*(k) \cdot (C^*(k, z_1^*) - C_M^*)}{\frac{1}{4} \cdot v^*(\frac{1}{2}) \cdot r^*(k + \frac{1}{2}) \cdot (C^*(0, z_1^*) - C_M^*) \cdot (C^*(k, z_1^*) - C^*(k + 1, z_1^*))}
\]
(42)

Equation 42 may be used to determine the function \( p \), and thus the radial variation of the radial diffusivity, from experimental concentration and flow distribution data. Furthermore, the corresponding eigen values and eigen functions
may then be evaluated from the system of equations represented by Equation 21. These results in turn may be used to calculate Peclet numbers.

**Calculation of Peclet numbers**

Consider an axial distance $z^*_g$ such that several or all terms in Equation 32 must be used to accurately describe the radial concentration distribution. Using the experimental concentration data measured at $z^*_g$ and imposing the orthogonality properties of the eigen functions, the following expression may be formed:

$$
\sum_{k=0}^{N} v^*(k) \cdot r^*(k) \cdot R_n(k) \cdot C^*(k, z^*_g) = 
$$

$$
C_n^* \cdot B_n \cdot Z_n(z^*_g) \cdot \sum_{k=0}^{N} v^*(k) \cdot r^*(k) \cdot R_n^2(k) 
$$

(43)

where $B_n$ is given by Equation 31 and the eigen functions are those associated with the $p$ function in question. Substituting the functional value of $Z_n(z^*_g)$ as given by Equation 14 and rearranging gives

$$
Pe_r(r^*_p) = \frac{d^*_p \cdot \beta_n \cdot v^*(r^*_p) \cdot z^*_g}{Q_n \cdot \left( \frac{C_n \cdot d^*_p}{z^*_g \cdot Pe_Z} - 1 \right)} 
$$

(44)

where
\[
Q_n = \ln \left[ \frac{\sum_{k=0}^{N} v^*(k) \cdot r^*(k) \cdot R_n(k) \cdot C^*(k, z^*_s)}{Q_n^* \cdot B_n \cdot \sum_{k=0}^{N} v^*(k) \cdot r^*(k) \cdot R_n^2(k)} \right].
\] (45)

Equation 44 holds for any \( n > 0 \). Thus there are \( N \) independent linear equations in \( \text{Pe}_r(\text{r}^*_p) \) and \( \text{Pe}_z \). Solving the resulting equations where \( n \) is successively one and two gives

\[
\text{Pe}_z = \frac{z^*_s}{\beta_1 \cdot \beta_2} \left( \frac{\beta_1 \cdot Q^2_2 - \beta_2 \cdot Q^2_1}{\beta_1 \cdot Q_2 - \beta_2 \cdot Q_1} \right).\] (46)

The numerical value for \( \text{Pe}_z \) calculated here is then used in Equation 44 in order to calculate \( \text{Pe}_r(\text{r}^*_p) \).

Prediction of Concentration Distributions

When the preceding methods are used to calculate \( p \), \( \text{Pe}_z \), and \( \text{Pe}_r(\text{r}^*_p) \) from experimental data, one is not assured that the reverse procedure will reproduce exactly the original concentration distributions. It is interesting to compare the distributions as predicted by Equation 32 using calculated values of \( p \), \( \text{Pe}_z \), \( \text{Pe}_r(\text{r}^*_p) \), and the associated eigen values and functions with the original experimental concentration data. The degree of agreement of the two represents to some extent a measure of the validity of the boundary value problem as a model for describing the mass transfer process.

Equation 32 may also be used to indicate the effect of neglecting axial transfer on the prediction of concentration distributions. When axial transfer is neglected, the func-
tional value of $Z_n(z^*)$ becomes

$$Z_n(z^*) = \exp \left[ - \frac{d_p^* \cdot \beta_n \cdot v^*(r_p^*)}{\text{Pe}_n(r_p^*)} \cdot z^* \right]$$  \hspace{1cm} (47)$$

and Equation 44 reduces to

$$\text{Pe}_n(r_p^*) = - \frac{d_p^* \cdot \beta_n \cdot v^*(r_p^*) \cdot z_s^*}{Q_n}.$$  \hspace{1cm} (48)$$

Thus the effective radial Peclet number may be calculated directly for the case $n = 1$. This value of $\text{Pe}_n(r_p^*)$ may then be used in Equation 32 where the functional value of $Z_n(z^*)$ is given by Equation 47 to predict the concentration distribution for the case when axial transfer is neglected.
RESULTS AND DISCUSSION

The scope of this investigation was chosen such that the effect of neglecting axial transfer on the prediction of concentration distributions would most likely be significant. The flow rate range includes points in the upper transition region just below the accepted fully developed turbulent region and those which are perhaps in the lower flow region of practical engineering applications.

Experimental Concentration Data

The experimental data consist of radial concentration distributions for various axial distances downstream from a centrally located tracer injector. Typical distributions are shown in Figure 5. The experimental data are tabulated in Table 6.

During experimentation the ambient temperature and the water temperature changed from day to day. These changes were indicated by the effluent stream temperature variations. The temperature data reported in Table 6 represent the range of the temperature of the effluent stream for all experiments performed for each particular flow rate. These data were considered only in the determination of the kinematic viscosity used to calculate the Reynolds numbers. Although the temperature is known to have some effect on the rate of mass transfer, this effect was not considered herein since the
Figure 5. Typical concentration data
overall temperature range was only 6.5°C.

The accuracy of the individual concentration determinations depended essentially on the reproducibility of the calibration of the colorimeter. The calibration was obtained by determining the transmittances for standard concentrations covering the range of interest. Periodic checks indicated that the transmittance could be reproduced with a maximum deviation of approximately 3 per cent of its mean value for all concentration levels.

Final consideration of the experimental data concerns its representation of the overall mass transfer process. Bernard and Wilhelm (7) repacked and hammered the test section until the single diameter traversed resulted in a fairly symmetrical concentration profile. Average values of the radial diffusivity and Peclet number were then calculated by applying a least squares technique to the data. Such a procedure, however, may not yield representative parameters of the overall mass transfer process.

Later investigators (21, 24, 34) found that concentrations in a packed bed varied not only from void to void but also within an individual interstice. Concentrations of samples removed from points on different radii but corresponding to the same radial position were found to be distributed randomly about a mean concentration which may be said to be characteristic of that radial position for the
particular experimental conditions. Preliminary experiments of this investigation yielded similar data. Figure 6 shows the extent of these variations for two diameters 60 degrees apart. Although these data were obtained when 0.384-inch packing was in the column, similar results may be expected for the 0.262-inch packing presently being considered.

Comparison of the concentration variations encountered in this work with those reported by others (21, 24, 34) show that the present variations are more extreme. This may be expected because of the combined effects of the very small molecular diffusion coefficient and the low flow rates investigated.

Fahien (24) concluded that concentration distributions representative of the overall mass transfer process may be obtained by averaging the concentrations from several equiangular positions for each radial position. A similar procedure was used in this study. However, in order to reduce the time necessary to obtain the large number of individual samples required, the multiple probe device was designed. With this device one could simultaneously obtain samples for several radial positions. In turn, the sample corresponding to each radial position was a mixture of samples removed from several angular positions. Concentration distributions obtained in this manner could then be analyzed in terms of a model assuming angular symmetry.

The reproducibility of concentration distributions
Figure 6. Variation of concentration with radial and angular position
obtained using the multiple probe device is of the same magnitude as that of previous investigators (21, 24) who used a single probe. Figure 7 indicates the deviations that may be expected for the data of this investigation.

To analyze experimental data by the previously described procedures, one needs values of the concentration at equally spaced radial positions. Since the experimental concentrations were not established at equally spaced positions and because of the scatter of the data, a smoothing process was used to obtain the data in the proper form. The data were plotted as shown in Figure 5, and appropriate values of the concentration were read from the smooth curves. For this work the radius was divided into ten equal increments. The smoothed data used in the calculations are tabulated in Table 5.

Flow Distribution

The superficial flow distribution was needed for the analysis of the concentration data. Experimental data for liquid systems are limited (14, 36), and those available are for particle and column diameters other than those used in this study. However, gas flow data are more complete (4, 21, 51). Dorweiler (21), using a five-loop hot-wire anemometer, measured flow distribution data for air flowing through a 4.026-inch i.d. column packed with 0.262-inch diameter
Figure 7. Reproducibility of concentration distributions
pellets. He found that the flow distribution deviated significantly from a uniform distribution and was essentially independent of flow rate above a mean superficial velocity of 0.4 foot per second (Re = 50). His data were used to develop the flow distribution needed for this work. Such usage assumes that the flow distributions for both gases and liquids are identical under similar flow conditions.

Qualitatively, the flow distribution may be described from considerations of the void fraction and the frictional force exerted by the column wall on the fluid. If only void fraction is considered (48, 50), the velocity distribution would be nearly uniform in the central section of the column, increasing on either side as the wall is approached. However, the frictional force exerted by the wall causes the velocity to decrease and thus approach a zero value right at the wall surface. This concept is in general agreement with the experimental data and is used herein to develop a quantitative expression for the flow distribution.

One could plot the experimental data points and draw a smooth curve through them. However, because only five points were available, such a technique might result in assigning unequal weight to each of the points. To avoid this possibility the data were fitted to an empirical expression which embodied the general concept outlined above. The expression used was
\[ v^* = A(1 - r^{*n}) + B(1 - r^{*m}) \] 

(49)

where the constants \( A, B, m, \) and \( n \) were determined by a least-squares method.

In order to satisfy the overall material balance requirements the integral equation

\[ \int_0^1 v^* r^* \, dr = \int_0^1 \left[ A(1 - r^{*n}) + B(1 - r^{*m}) \right] r^* \, dr^* = \frac{1}{2} \] 

(50)

must be satisfied. Integrating and rearranging gives

\[ A = \left( \frac{n + 2}{n} \right) (1 - \frac{mB}{m + 2}) \] 

(51)

The criterion for determining \( B, n, \) and \( m \) was to minimize the sum of the squares of the differences between the experimental data points (Table 4) and the values represented by Equation 49. This sum is

\[ S = \sum_{j=1}^{5} \left[ \left( \frac{n + 2}{n} \right) (1 - \frac{mB}{m + 2}) (1 - r_j^{*n}) + B(1 - r_j^{*m}) - v_j^* \right]^2 \] 

(52)

\( S \) was minimized with respect to \( B \), the "best" value of \( B \) being the solution of the equation

\[ \frac{\partial S}{\partial B} = 0 \] 

(53)

for a given \( n \) and \( m \). The final \( n \) and \( m \) were established by determining the combination which resulted in minimizing \( S \).

The ranges of \( n \) and \( m \) were: \( 2 \leq n \leq 36, 4 \leq m \leq 38, n \neq m \).

All combinations of even \( n \) and \( m \) were tried within these
ranges. The calculations were performed by an IBM 7074 digital computer.

The final working equation is

\[ v^* = -9.0737(1 - r^8) + 9.6355(1 - r^{12}) \]  

A graph of this equation is given in Figure 8. The only criterion for evaluating the validity of using this flow distribution is the deviation of the integral mean concentrations (Equation 27) from their theoretical value of unity. The average deviation was 7.0 per cent with a maximum deviation of 13.8 per cent as indicated in Table 5.

Radial Variation of Diffusivities

Axial diffusivity

The assumption of a constant axial Peclet number was necessary for the solution of the boundary value problem. This was tantamount to assuming that the point axial diffusivity is proportional to the point superficial velocity. Thus the radial variation of the axial diffusivity is depicted by the flow distribution given in Figure 8. Such a variation may be readily theorized. However, because quantitative information about the axial diffusivity is quite limited, the evaluation of its magnitude (and thus Pe_z) necessarily takes precedence over the determination of its variation with radial position. This is the primary justifi-
Figure 8. Superficial flow distribution

\[ v^* = -9.0737(1-r^*8) + 9.6355(1-r^*2) \]
cation for assuming a constant axial Peclet number in this study.

**Radial diffusivity**

The variation of the radial diffusivity with radial position is shown in Figure 9. This variation was established from calculations (Appendix A) in which the smoothed concentration data for the following conditions were used: $Re' = 84.9$, $z = 32.0$ inches. These data satisfied the requirement that they could be accurately described by Equation 3.3.

The variation of $p$ given in Figure 9 was used for the entire flow rate range. Fahien (24) found that for the carbon dioxide-air system the radial variation of the radial diffusivity was independent of flow rate. Dorweiler and Fahien (22) later showed that the variation was not independent of flow rate for rates corresponding to Reynolds number below approximately 100. This dependency exists as a result of the increasing molecular contribution to the overall transfer process at low Reynolds numbers. Since the molecular diffusion coefficient for liquids is on the order of one ten-thousandth of that for gases, such a dependency may be expected in liquid systems only at much lower Reynolds numbers.

It is interesting to compare the variation of the radial diffusivities with radial position for gases and liquids. Both Fahien (24) and Dorweiler (21) found greater variations
Figure 9. Variation of radial diffusivity with radial position
for gases than for the liquid data presented herein. For comparison purposes the average variation for the carbon dioxide-air system over the flow range \( 24.7 \leq Re' \leq 484 \) is also given in Figure 9. This variation was determined by arithmetically averaging the values at each radial position for the seven flow rates reported by Dorweiler (21).

Peclet Numbers

**Axial Peclet numbers**

Calculated axial Peclet numbers are shown graphically in Figure 10. Since the results scatter so much, it is difficult to determine a significant trend. This scatter is perhaps indicative of the sensitivity of the calculations. The sensitivity is best illustrated by the sample calculation given in Appendix A.

The effect of the variation of the radial diffusivity with radial position on the axial Peclet number was determined. Calculations were made for the following functional values of \( p \):

1. \( p = \text{calculated } p(r^*) \text{ as given in Figure 9.} \)
2. \( p = 1.0; \text{ i.e., } Er \text{ is a constant.} \)
3. \( p = K \cdot v^*; \text{ i.e., } Er \text{ varies as the superficial flow distribution.} \)
Figure 10. Calculated axial Peclet numbers

\[ p = \text{CALCULATED } p(r^*) \]

MEAN = 0.1575
4. $p = 1.0$, $v^* = 1.0$; in addition to assuming a constant radial diffusivity, the flow distribution was also assumed uniform across the radius.

The first case resulted in values approximately 5 percent greater than those of the second. The results for these two cases are tabulated in Table 3. Calculations for the last two cases resulted in either negative values for the axial Peclet numbers or negative quantities inside the brackets in Equation 45. Such results are to some extent indicative of the lack of validity of these two models as descriptive of the physical situation.

The results of this study are compared in Figure 11 with those of representative investigations concerned with the unsteady-state axial dispersion of liquids and gases flowing through fixed beds of particles (23, 41). Axial Peclet numbers have not previously been calculated from steady-state data for either gases or liquids flowing through fixed beds. It is interesting that there is such close agreement between the liquid dispersion results and the present results since the axial dispersion model Peclet number accounts for, in addition to turbulent mixing and molecular diffusion, the effect of a non-uniform flow distribution. This agreement apparently supports the belief of many investigators (11, 13, 15, 23, 39, 40, 41, 54) that the axial dispersivity is primarily a measure of the axial transfer process.
Figure 11. Correlation of axial Peclet number with Reynolds number
An analysis by Gottschlich (26) indicated that the discrepancy between axial dispersion Peclet numbers for gases and liquids may be explained by considering a stagnant film which affects axial dispersion only in unsteady-state processes. He concluded that for a steady-state process, such as a catalytic reactor, the axial dispersion Peclet number should be approximately 2.0, whether for gas or liquid systems. The results herein, on the other hand, appear to contradict this explanation. A more acceptable explanation, although lacking direct experimental evidence, is that the greater degree of axial mixing for liquid systems results from the increased by-passing, trapping, and short-circuiting of large liquid packets at low Reynolds numbers. At higher Reynolds numbers the values of the axial Peclet number for liquids would approach those for gases since greater turbulence should cause a higher degree of mixing in the void spaces, hence less by-passing and short-circuiting of large fluid packets, and thus less axial mixing for the system as a whole.

Radial Peclet numbers

Radial Peclet numbers are shown in Figure 12 as a function of Reynolds number. If axial transfer is neglected in the analysis of the experimental data, the resulting calculated effective radial Peclet numbers are seen to be 5–10 per
Figure 12. Effect of neglecting axial transfer on radial Peclet number

- ○ AXIAL TRANSFER INCLUDED
- △ AXIAL TRANSFER NEGLECTED

\[ p = \text{CALCULATED } p(r^*) \]
cent less than for the case when it is included. These results, tabulated in Table 3, are in general agreement with those of Roemer et al. (49) for gases.

Values of the radial Peclet number were determined assuming the four functional values for the radial diffusivity described previously. The results, tabulated in Table 3, may be summarized as follows: values for case 4 > values for case 3 > values for case 1 > values for case 2.

Figure 13 compares the radial Peclet numbers of this study with those of Dorweiler (21) for gases. Fahien (24) and Dorweiler (21) are the only previous investigators to consider radial variations of radial diffusivity and flow distribution in the analysis of fixed-bed mass transfer data. Both neglected axial transfer in their analyses of gas-flow systems.

The values of the radial Peclet number for liquids approach those for gases at the higher Reynolds numbers. This phenomenon was first demonstrated by Latinen (37) when he compared his liquid-flow results with those of Bernard and Wilhelm (7) for gas-flow systems. The close agreement between the two systems at the higher Reynolds numbers shows that physical properties of the fluid have little effect on the value of the radial Peclet number. At lower Reynolds numbers, however, as the turbulent contribution to mass transfer diminishes, the two correlations diverge for the results shown. This
Figure 13. Correlation of radial Peclet number with Reynolds number
divergence arises because the molecular diffusion coefficient for gases is on the order of ten thousand times greater than that for liquids. The gas-flow radial Peclet number reaches a maximum and then decreases with Reynolds number as the turbulent effect damps out, ultimately reaching a linear relationship with Reynolds number. One may expect a similar effect in the liquid-flow correlation, although at a much lower flow rate.

Prediction of Concentration Distributions

One test of the validity of mass transfer models is to compare the predicted concentration distributions for each model with those of others and with experimental data. Predicted concentration distributions for the diffusivity models previously described are compared graphically in Figures 14 through 18. Figure 20 illustrates the agreement between the diffusivity model and a two-dimensional finite stage model.

Comparison of diffusivity models

Figures 14 and 15 show the effect of neglecting axial transfer on the prediction of concentration distributions. The infinite axial Peclet number represents the case when axial transfer is neglected. Except for the central portion of the distributions the effect is quite small. Even the discrepancy near the center is not large (≈ 10 per cent).
Figure 14. Effect of neglecting axial transfer on concentration distribution
Figure 15. Effect of neglecting axial transfer on concentration distribution.
The larger discrepancy near the center becomes quite acceptable when one realizes that the flow in the central portion of the bed is a very small fraction of the total flow. For example, the flow in the portion of the bed represented by \(0 \leq r^* \leq 0.3\) is approximately 5 per cent of the total flow; i.e.,

\[
\frac{\int_0^{0.3} v^* r^* dr^*}{\int_0^1 v^* r^* dr^*} \approx 0.05 .
\]

(55)

Although axial transfer is seen to be of little importance in this study, even at very low flow rates, one may not necessarily neglect it when designing chemically reactive systems in which axial concentration gradients may be extremely large.

Figures 16 and 17 show the deviations between predicted concentration distributions for the calculated radial variation of the radial diffusivity and for a constant radial diffusivity. The small deviations (generally less than 1 per cent) should perhaps be expected since the calculated diffusivity variation is not very great across most of the radius as shown in Figure 9.

Figure 18 summarizes the effects of the four radial diffusivity models described previously on the prediction of concentration distributions. A cursory inspection indicates that all four models may be acceptable. However, here the
Figure 16. Effect of radial variation of radial diffusivity on concentration distribution
Figure 17. Effect of radial variation of radial diffusivity on concentration distribution.
Figure 18. Effect of variable radial diffusivity and velocity on concentration distribution
graphical test of the models must be supplemented. First, the assumption of a uniform flow distribution in case 4 does not result in acceptable material balances; i.e., the calculated values of \( C_M^* \) are in very poor agreement with the theoretical value of unity (Table 5). Second, for cases 3 and 4 no axial Peclet number could be calculated. It is true that for this work axial transfer appears to be of little importance. However, the practical value of this study lies in the utility of the various mass transport parameters for designing chemical engineering equipment, and in particular, equipment for chemically reactive systems. The importance of considering axial transfer in these systems has not been fully established. And finally, Richardson (46), in a recent study, showed that case 1 resulted in the best agreement between experimental and calculated mean conversions for the oxidation of sulfur dioxide in a fixed-bed catalytic reactor. The next best agreement was obtained for case 4 and the poorest agreement was obtained for case 3.

**Comparison of diffusivity and finite stage models**

Deans and Lapidus (18) developed a mathematical model for predicting the mixing characteristics of fixed beds of spheres. The model is based on a two-dimensional network of perfectly mixed stages. A material balance about a general stage provides a working equation for determining the concen-
tration in that stage from concentrations of previous stages.

The model is developed assuming that angular flow is absent and that the void fraction and the flow distribution are independent of position in the bed. Each stage represents the voids contained in an angular disk, of which only a segment is shown in Figure 19. The stage with indices \(i, j\) includes the voids in the volume bounded 1) by two planes at distances \((i-1)\)d and \(id\) from the inlet end of the bed, and 2) by two concentric cylinders of radius \(K'(j-1)d\) and \(K'jd\). The number of stages in the axial direction is given by \(N = z/d\), assumed integral. The arrangement of stages shown in Figure 19 is obtained by letting \(j\) take on the values \(1/3, 3/2, 5/2, \ldots, K+1/2\) when \(i\) is an odd integer, and the values 1, 2, 3, \ldots, \(K\) when \(i\) is even. The constant \(K'\) represents the multiple of half-particle diameters which the fluid side-steps in an actual bed. It is evaluated from consideration of the particular flow conditions. The net work is set up such that either the even or odd rows (but not both) will have fractional stages at the wall.

The original model is modified herein to include a radial variation of the flow distribution. Thus, the general expression for the concentration in a stage may be written

\[
C_{i,j} = \frac{(C_{i-1,j-1/2})(\bar{v}_{i-1/2})(j-3/4) + (C_{i-1,j+1/2})(\bar{v}_{i+1/2})(j-1/4)}{\left(\bar{v}_{j}\right)(2j-1)}
\]

(56)
Figure 19. Schematic representation of the arrangement of stages for the finite stage mass transfer model.
From Figure 17 it is easily seen that the flow through a given stage is the sum of partial flows from each of the two preceding stages. In order that the total flow be conserved, it is necessary to accurately define the mean dimensionless velocities in Equation 56. This is done mathematically by the following expressions:

\[
\overline{v}_{j-1/2} = \frac{\int_{r_j-1/2}^{r_j} v^* r^* dr^*}{\int_{r_j-1/2}^{r_j} r^* dr^*} \quad \text{(57)}
\]

\[
\overline{v}_{j+1/2} = \frac{\int_{r_j}^{r_j+1/2} v^* r^* dr^*}{\int_{r_j}^{r_j+1/2} r^* dr^*} \quad \text{(58)}
\]

\[
\overline{v}_j = \frac{\int_{r_{j-1/2}}^{r_j+1/2} v^* r^* dr^*}{\int_{r_{j-1/2}}^{r_j+1/2} r^* dr^*} \quad \text{(59)}
\]
For the particular case $j = 1/2$ it is easily seen from Figure 17 that

$$C_{i,1/2}^* = C_{i-1,1}^* \ (60)$$

If the radius is divided into an integral number of stage widths, the equation for the fractional stage at the wall is seen to be

$$C_{i,M+1/2}^* = C_{i=1,M}^* \ (61)$$

Simulation of the experimental system used in this study was readily accomplished by the use of the finite stage model. The steady-state concentrations of all stages in an arbitrary network are given by Equations 56, 60, and 61. The only external condition required is the stipulation of the tracer concentration in the inlet stream, which is given by

$$C_{i,1/2}^* = q \ (62)$$

where $q$ is arbitrary. For comparison purposes $q$ was chosen such that $C_M^*$ was unity. Mathematically,

$$q = \frac{\int_{0}^{1} v^* r^* dr^*}{\int_{r_j=1/2}^{r_{j=1/2}} v^* r^* dr^*} \ (63)$$

Other parameters chosen were $M = 8$ and $N = 271$. The value of $M$ was calculated from the relation
M = \frac{d_0}{2d_p K'} = \frac{d_0}{2d_p \sqrt{8.2 \text{Pe}(r_p^*)}}, \quad (64)

a modification of that suggested by Deans and Lapidus (18) to bring the model into agreement with any given experimental value of \( \text{Pe}(r_p^*) \). Stage concentrations were calculated using an IBM 7074 digital computer. These concentrations were compared with concentration distributions generated by Equation 32 for the diffusivity model of variable radial diffusivity.

Graphical comparison of the two models is made in Figure 20. The diffusivity model concentration distributions at axial distances of 15.5 and 32.0 inches from the tracer injector are in good agreement with those for the finite stage model at the 46th and 95th axial stages, respectively. The axial stage length may be calculated thusly:

\[ L = \frac{15.5 \text{ inches}}{46-1} \approx \frac{32.0 \text{ inches}}{95-1} \approx 0.34 \text{ inches}. \quad (65) \]

The original statement of the finite stage model assigns the axial length of a stage a value of \( d_p \) (in this study \( d_p = 0.262 \text{ inches} \)). This discrepancy may be partially accounted for by the method in which Equation 64 was derived (18). In any event this degree of success of such a simple model in predicting concentration distributions certainly indicates its potential as a basis for a highly accurate model for representing the mass transport process in a packed bed.
Figure 20. Comparison of finite stage and diffusivity models.
SUMMARY AND CONCLUSIONS

The major results of this study may be summarized as follows:

1. Concentration distributions were measured for a tracer material being transported in a main stream of water flowing slowly (Re' < 100) through a packed bed of spherical particles.

2. Axial and radial Peclet numbers were determined from the data of a single experiment.

3. Values of the axial Peclet number were found to be on the order of one-hundredth those of the radial Peclet number; hence, the axial diffusivity is approximately one hundred times greater than the radial diffusivity for the conditions of this investigation.

4. Although the axial diffusivity was found to be much larger than the radial diffusivity, the effect of including axial transfer in the prediction of concentration distributions was shown to be quite small. However, for chemically reactive systems, in which large axial concentration gradients may exist, axial transport may be significant.

5. The variation of the radial diffusivity with radial position was found to be much less pronounced than that for gas-flow systems as determined by previous investigators.

6. The empirical equation used to correlate flow distribution data for gases appears to adequately represent the
flow distribution for liquids in fixed beds of identical physical configuration. The sole basis for this conclusion is the good agreement between the calculated integral mean concentrations and their theoretical value of unity.
### NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>constant in flow distribution equation</td>
</tr>
<tr>
<td>A(k)</td>
<td>matrix notation used in numerical solution of Sturm-Liouville problem</td>
</tr>
<tr>
<td>A'_n</td>
<td>constant in series solution</td>
</tr>
<tr>
<td>B</td>
<td>constant in flow distribution equation</td>
</tr>
<tr>
<td>B'_n</td>
<td>modified constant in series solution</td>
</tr>
<tr>
<td>B_l(k)</td>
<td>matrix notation used in numerical solution of Sturm-Liouville problem</td>
</tr>
<tr>
<td>C</td>
<td>concentration of transferring material</td>
</tr>
<tr>
<td>C_E</td>
<td>measured steady-state mean concentration in the column</td>
</tr>
<tr>
<td>C*</td>
<td>dimensionless concentration, C/C_E</td>
</tr>
<tr>
<td>C_i</td>
<td>dimensionless concentration of tracer material</td>
</tr>
<tr>
<td>C_i,j</td>
<td>dimensionless concentration in the i,j stage of finite stage model</td>
</tr>
<tr>
<td>C_M</td>
<td>integral mean concentration, defined by Equation 27</td>
</tr>
<tr>
<td>D</td>
<td>molecular diffusion coefficient</td>
</tr>
<tr>
<td>D(k)</td>
<td>matrix notation used in numerical solution of Sturm-Liouville problem</td>
</tr>
<tr>
<td>D_L</td>
<td>total effective axial &quot;diffusivity&quot; or dispersivity</td>
</tr>
<tr>
<td>d</td>
<td>differential operator</td>
</tr>
<tr>
<td>d_o</td>
<td>column diameter</td>
</tr>
<tr>
<td>d_p</td>
<td>mean packing diameter</td>
</tr>
<tr>
<td>d_p*</td>
<td>dimensionless particle diameter, d_p/r_o</td>
</tr>
<tr>
<td>E</td>
<td>effective diffusivity, a scalar quantity</td>
</tr>
<tr>
<td>E_i,j</td>
<td>component in total diffusivity tensor; i = r,(\phi),z; j = r,(\phi),z</td>
</tr>
</tbody>
</table>
$E_r$  radial diffusivity, $E_{rr}$

$E_r(r_p^*)$  radial diffusivity evaluated at $r_p^*$

$E_{ij}$  component in turbulent diffusivity tensor; $i = r, \phi, z$; $j = r, \phi, z$

$E_z$  axial diffusivity, $E_{zz}$

$E$  total diffusivity tensor

$E_{tt}$  turbulent diffusivity tensor

$h$  dimensionless radial increment length, $1/N$

$I$  unit matrix

$I = I$  unit second-order tensor

$i$  designation of axial position of stage in finite stage model

$J$  mass transfer flux vector

$J$  designation of radial position of stage in finite stage model; summation index

$K$  proportionality constant

$K'$  multiple of half-particle diameters which the fluid side-steps in an actual bed

$k$  point of division in dimensionless radius, $k = 0, 1, \ldots N$

$L$  axial length of stage in finite stage model

$M$  whole number of stages across radius in finite stage model

$m$  correlation function; subscript indicating an arbitrary eigen function; exponent in flow distribution equation

$N$  total number of increments of division in $0 \leq r^* \leq 1.0$; number of stages in axial direction in finite stage model

$n$  subscript indicating an arbitrary eigen value and its corresponding eigen function; exponent in flow distribution equation; correlation function
Pe: general Peclet number, $dpV/E$

$Pe_r(r^*_p)$: radial Peclet number evaluated at $r_p$, $dpu_z(r_p)/Er(r_p)$

$Pe_z$: axial Peclet number, $dpu_z(r)/E_z(r)$

$Pe'_z$: axial Peclet number, $dpV/DL$

$Pe''_z$: axial Peclet number, $dpU/DL$

$r$: radial variation of $Er$, $Er(r)/Er(r^*_p)$

$q$: symbol for expression given in Equation 45

$Q_n$: dimensionless tracer concentration in the inlet stream of the finite stage model

$R$: solution to Sturm-Liouville problem

$Re'$: Reynolds number, $dpV/(\mu/\rho)$

$Re''$: line Reynolds number, $dpV/\epsilon (\mu/\rho)$

$R_n(k)$: eigen function

$r$: radial coordinate; radial distance from center of packed column

$r_1$: radius of injection tube

$r_0$: radius of column

$r_p$: a specified radial position

$r^*$: dimensionless radial position, $r/r_0$

$r^*_1$: dimensionless radius of injection tube, $r_1/r_0$

$r^*_p$: dimensionless $r_p$, $r_p/r_0$

$S$: symbol for sum given in Equation 52

$T_E$: measured mean temperature of effluent stream

$t$: time

$U$: mean interstitial velocity, $V/\epsilon$

$u_z$: axial component of superficial velocity vector
$u$ superficial velocity vector

$V$ mean superficial velocity, based on empty column cross section

$v^*$ dimensionless flow distribution, $u_z(r)/V$

$v^*(r_p^*)$ dimensionless flow distribution evaluated at $r_p$

$\bar{v}^*_j$ mean dimensionless velocity defined by Equations 57, 58, and 59

$Z$ particular solution of Equation 12

$z$ axial coordinate; axial distance from tracer injection tube

$z^*$ dimensionless axial position, $z/r_o$

$z_1^*$ large dimensionless axial distance from the injection tube

$z_s^*$ small dimensionless axial distance from the injection tube

$\beta$ a real positive number

$\beta_n$ eigen value

$\nabla$ gradient operator

$\partial$ partial differential operator

$\epsilon$ mean void fraction in packed column

$\mu/\rho$ fluid kinematic viscosity

$\Sigma$ summation symbol

$\phi$ angular coordinate

$\int$ integration symbol
LITERATURE CITED


38. Levenspiel, O. and Bischoff, K. B. Fluid dispersion. [To be published in Advances in Chemical Engineering Volume 4 ca. 1964].


Calculation of the radial variation of $p$

The radial variation of the function $p$ was calculated using smoothed concentration data (Table 5) for the following experimental conditions: $Re' = 84.9$, $z = 32.0$ inches. The details are presented in Table 2. For the purposes of this calculation only, the following shorthand symbols are defined:

\[
\begin{align*}
    r^*_k &= r^*(k) \\
    v^*_k &= v^*(k) \\
    p_k &= v^*(k) \cdot r^*(k) \\
    C^*_k &= C^*(k, 32.0 \text{ inches})
\end{align*}
\]

The integral mean concentration is given by

\[
C_M^* = \frac{\sum_{k=0}^{10} p_k C_k}{\sum_{k=0}^{10} p_k} = \frac{4.95320}{4.98660} = 0.9933.
\]

As indicated in Equation 42, $p$ is evaluated at each internal one-half interval of $k$. For example, when $k = 3$, $p$ is evaluated at $r^*_3 \ 1/2$ or $r^* = 0.35$ since $h = 0.10$:

\[
p(3 \ 1/2) = \frac{(0.025)(0.25003)}{(0.25)(0.56180)(0.35)(0.8667)(0.139)} = 1.0564.
\]
Table 2. Calculation of the radial variation of p

<table>
<thead>
<tr>
<th>k</th>
<th>r^*k</th>
<th>v^*k</th>
<th>Ck*</th>
<th>Pk</th>
<th>PkCk*</th>
<th>Ck*-Ck*(Ck*-Ck*)</th>
<th>Pk</th>
<th>( \sum P_k)</th>
<th>Ck*</th>
<th>Ck*-b</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.00</td>
<td>0.56180</td>
<td>1.860</td>
<td>0.00702</td>
<td>0.01306</td>
<td>0.0667</td>
<td>0.00608</td>
<td>0.030</td>
<td>0.025</td>
<td>1.00000</td>
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<tr>
<td>1</td>
<td>0.05</td>
<td>0.56180</td>
<td>1.830</td>
<td>0.05618</td>
<td>0.10281</td>
<td>0.8367</td>
<td>0.04700</td>
<td>0.070</td>
<td>0.072</td>
<td>1.01048</td>
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<td>2</td>
<td>0.20</td>
<td>0.56180</td>
<td>1.760</td>
<td>0.11236</td>
<td>0.19775</td>
<td>0.7667</td>
<td>0.08615</td>
<td>0.139</td>
<td>0.110</td>
<td>1.04091</td>
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<tr>
<td>3</td>
<td>0.30</td>
<td>0.56239</td>
<td>1.650</td>
<td>0.16879</td>
<td>0.27839</td>
<td>0.6567</td>
<td>0.11080</td>
<td>0.25003</td>
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<td>0.139</td>
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<td>4</td>
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<td>0.5167</td>
<td>0.11731</td>
<td>0.35734</td>
<td>0.155</td>
<td>0.158</td>
<td>1.06209</td>
</tr>
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<td>5</td>
<td>0.50</td>
<td>0.59439</td>
<td>1.350</td>
<td>0.29745</td>
<td>0.40304</td>
<td>0.3517</td>
<td>0.10759</td>
<td>0.47493</td>
<td>0.120</td>
<td>0.167</td>
<td>1.06312</td>
</tr>
<tr>
<td>6</td>
<td>0.80</td>
<td>0.89323</td>
<td>1.175</td>
<td>0.41594</td>
<td>0.48873</td>
<td>0.1817</td>
<td>0.07559</td>
<td>0.55051</td>
<td>0.175</td>
<td>0.183</td>
<td>1.08826</td>
</tr>
<tr>
<td>7</td>
<td>0.70</td>
<td>0.95151</td>
<td>1.000</td>
<td>0.66606</td>
<td>0.66606</td>
<td>0.0067</td>
<td>0.00446</td>
<td>0.55497</td>
<td>0.130</td>
<td>0.142</td>
<td>1.07134</td>
</tr>
<tr>
<td>8</td>
<td>0.80</td>
<td>1.42197</td>
<td>0.870</td>
<td>1.13758</td>
<td>0.92969</td>
<td>0.1233</td>
<td>0.14026</td>
<td>0.41471</td>
<td>0.090</td>
<td>0.102</td>
<td>1.08335</td>
</tr>
<tr>
<td>9</td>
<td>0.90</td>
<td>1.74638</td>
<td>0.780</td>
<td>1.57174</td>
<td>1.22586</td>
<td>0.2133</td>
<td>0.33525</td>
<td>0.07946</td>
<td>0.031</td>
<td>0.042</td>
<td>1.09333</td>
</tr>
<tr>
<td>10</td>
<td>1.00</td>
<td>0.00000</td>
<td>0.750</td>
<td>0.36652</td>
<td>0.24489</td>
<td>0.2433</td>
<td>0.07944</td>
<td>0.00002</td>
<td>4.98660</td>
<td>4.95320</td>
<td></td>
</tr>
</tbody>
</table>

aCalculated using Equation 54.

bValues of Ck*-Ck*+1 were plotted at the one-half intervals of k as shown in Figure 21. These values of Ck*-Ck*+1 used in the calculations were read from the smooth curve drawn.

cCalculated using Equation 17.

dCalculated using Equation 19.
Figure 21. Smoothing of concentration differences
Calculation of Peclet numbers

The axial and radial Peclet numbers were calculated using Equations 46 and 44, respectively. The procedure is demonstrated here using the smoothed concentration data (Table 5) for the following experimental conditions: $Re = 84.9$, $z = 32.0$ inches. The case of the calculated $p$ function is considered.

The digital computer was used to calculate the associated eigen values and eigen functions and all the quantities inside the brackets of Equation 45. Then, for $n = 1,$

$$Q_1 = \ln \left[ \frac{0.14798}{(0.8878)(8.6678)(0.05622)} \right]$$

$$= -1.07285$$

and for $n = 2,$

$$Q_2 = \ln \left[ \frac{0.02411}{(0.8878)(11.522)(0.04023)} \right]$$

$$= -2.83729 .$$

Using Equation 46, for $n = 1$ and $n = 2,$

$$Pe_z = \frac{(0.14798)}{(1.985)} \left[ \frac{(20.4903)(-2.83729)^2 - (63.6384)(-1.07285)^2}{(15.5)(\frac{1}{1.985})} \right] \left[ (20.4903)(-2.83729) - (63.6384)(-1.07285) \right]$$

$$= \frac{(0.016903)(164.95130 - 73.24825)}{(-58.13692 + 68.27446)}$$

$$= 0.1529 .$$

Then using Equation 44 for $n = 1,$
The radial Peclet number is evaluated as \( r_p^* = 0.05 \) since \( h = 0.10 \), and \( r_p^* = h/2 \) from Equation 39.

When axial transfer is neglected the radial Peclet number may be calculated using Equation 48 for \( n = 1 \),

\[
\text{Pe}_r(0.05) = \frac{(0.262 \times 20.4903 \times 0.56180 \times 15.5)}{1.985} \left( \frac{-1.07285 \times 0.262}{1.985} - 1 \right) \frac{15.5}{1.985 (0.1529)}
\]

\[
= 9.8862 .
\]

The radial Peclet number is evaluated at \( r_p^* = 0.05 \) since \( h = 0.10 \), and \( r_p^* = h/2 \) from Equation 39.

When axial transfer is neglected the radial Peclet number may be calculated using Equation 48 for \( n = 1 \),

\[
\text{Pe}_r(0.05) = \frac{(0.262 \times 20.4903 \times 0.56180 \times 15.5)}{1.985} \left( \frac{-1.07285 \times 0.262}{1.985} - 1 \right) \frac{15.5}{1.985 (0.1529)}
\]

\[
= 11.0587 .
\]

The Peclet numbers are tabulated in Table 3.
### Tabular Results

Table 3. Summary of Peclet numbers for various models

<table>
<thead>
<tr>
<th>Re</th>
<th>z</th>
<th>p=calculated $\text{Pe}(r_p)$</th>
<th>$\text{Pe}(r^*)$</th>
<th>$\text{Pe}(r_p)^b$</th>
<th>p=1.0</th>
<th>$\text{Pe}(r_p)$</th>
<th>$\text{Pe}(r_p)^b$</th>
<th>$\text{Pe}(r_p)$</th>
<th>$\text{Pe}(r_p)^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\text{Per}(r_p)$</td>
<td>$\text{Pe}(r_p)$</td>
<td>$\text{Per}(r_p)$</td>
<td></td>
<td>$\text{Per}(r_p)$</td>
<td>$\text{Per}(r_p)^b$</td>
<td>$\text{Per}(r_p)$</td>
<td>$\text{Per}(r_p)^b$</td>
</tr>
<tr>
<td>7.1</td>
<td>32.0</td>
<td>27.5827 0.3214 28.1931</td>
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<td></td>
<td>26.1451 0.2778 26.8160</td>
<td>29.5619 36.1224</td>
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<td></td>
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<tr>
<td>11.2</td>
<td>32.0</td>
<td>24.7232 0.1966 25.7043</td>
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<td></td>
<td>23.5142 0.1952 24.4557</td>
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<tr>
<td>17.2</td>
<td>32.0</td>
<td>17.0309 0.0501 20.3759</td>
<td></td>
<td></td>
<td>16.1467 0.0490 19.3943</td>
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<td></td>
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</tr>
<tr>
<td>26.4</td>
<td>32.0</td>
<td>14.7597 0.0958 16.6188</td>
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<td></td>
<td>14.1696 0.1048 15.8048</td>
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<td></td>
<td></td>
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<tr>
<td>35.0</td>
<td>15.5</td>
<td>12.8565 0.0768 15.0822</td>
<td></td>
<td></td>
<td>12.1366 0.0724 14.3669</td>
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<tr>
<td>43.2</td>
<td>15.5</td>
<td>12.3835 0.0767 14.6018</td>
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<td></td>
<td>11.6990 0.0729 13.9075</td>
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<td>58.8</td>
<td>15.5</td>
<td>11.9073 0.2964 12.5492</td>
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<td>11.3010 0.2838 11.9325</td>
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<td>77.0</td>
<td>15.5</td>
<td>9.9336 0.1510 11.1193</td>
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<td>9.4207 0.1471 10.5779</td>
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<td>84.9</td>
<td>15.5</td>
<td>9.8862 0.1529 11.0587</td>
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<td></td>
<td>9.3866 0.1504 10.5206 11.9453 15.1242</td>
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<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Mean =**

0.1575 0.1504

*Axial Peclet numbers could not be calculated.*

*Axial transfer was neglected.*
Table 4. Flow distribution data (21)

<table>
<thead>
<tr>
<th>J</th>
<th>$r^*_j$</th>
<th>$v^*_j$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.3162</td>
<td>0.4408</td>
</tr>
<tr>
<td>2</td>
<td>0.5477</td>
<td>0.6167</td>
</tr>
<tr>
<td>3</td>
<td>0.7071</td>
<td>0.8009</td>
</tr>
<tr>
<td>4</td>
<td>0.8367</td>
<td>1.5125</td>
</tr>
<tr>
<td>5</td>
<td>0.9487</td>
<td>1.3287</td>
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</table>
Table 5. Smoothed values of C/CE used in calculations

<table>
<thead>
<tr>
<th>Re'</th>
<th>7.1</th>
<th>11.2</th>
<th>17.2</th>
<th>26.4</th>
<th>35.0</th>
<th>43.2</th>
<th>58.8</th>
<th>77.0</th>
<th>84.9</th>
</tr>
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<tbody>
<tr>
<td>r*</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>5.74</td>
<td>4.80</td>
<td>3.96</td>
<td>3.16</td>
<td>1.86</td>
<td>6.96</td>
<td>6.14</td>
<td>5.05</td>
<td>4.44</td>
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<td>3.81</td>
<td>3.06</td>
<td>1.83</td>
<td>6.66</td>
<td>5.79</td>
<td>4.80</td>
<td>4.20</td>
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<td>3.46</td>
<td>2.83</td>
<td>1.76</td>
<td>5.54</td>
<td>4.92</td>
<td>4.28</td>
<td>3.69</td>
</tr>
<tr>
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<td>2.97</td>
<td>2.495</td>
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<td>4.03</td>
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<td>3.02</td>
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<tr>
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<td>2.36</td>
<td>2.09</td>
<td>1.51</td>
<td>2.77</td>
<td>2.62</td>
<td>2.75</td>
<td>2.35</td>
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<td>1.18</td>
<td>1.70</td>
<td>1.98</td>
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<td>1.28</td>
<td>1.175</td>
<td>1.16</td>
<td>1.06</td>
<td>1.32</td>
<td>1.20</td>
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<td>1.00</td>
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Cf

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*Calculated assuming a uniform flow distribution.
Table 6. Experimental values of $C/C_5$

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\(^a\)The center concentrations for this axial level are arithmetic averages of three experiments.

\(^b\)Except for the center position each concentration is an arithmetic average of two or more experiments.
Table 6. (Continued)

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*No sample was taken.*
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APPENDIX B

The numerical solution of the Sturm-Liouville problem and some of the associated calculations with the experimental concentration data were performed by an IBM 7074 digital computer. The computer program was written in the FULL FORTRAN IBM language and was essentially a combination of three separate programs: the major program, the subroutine for calculating the eigen values (SUBROUTINE EIGN), and the subroutine for calculating the eigen functions (SUBROUTINE VCTR). The major variables used in the program in the order of their first appearance in the FORTRAN statements are defined as follows:

IDATA  a control integer defining the amount of input and giving a dump of the core memory if desired
JDATA  a control integer specifying the form (equation or tabular) of the input flow distribution
KDATA  a control integer specifying the form (equation or tabular) of the input p function
V1    constant in the flow distribution equation, A
V2    constant in the flow distribution equation, B
V3    constant in the flow distribution equation, generally zero
NX    exponent in the flow distribution equation, n
Mx    exponent in the flow distribution equation, m
F     constant in the p function equation; used only in the case 3 radial diffusivity model
G     constant in the p function equation; used only in the case 3 radial diffusivity model
SP exponent in the p function equation; used only in the case 3 radial diffusivity model

SQ exponent in the p function equation; used only in the case 3 radial diffusivity model

NN $2N+1$

KP number of eigen functions calculated

LV number of concentration distributions input

RINJ $r_1^*$

N $N+1$

N1 $N$

H $h$

R $r^*$

U $v^*$

P $p$

D matrix $D(k)$; later used as storage for newly calculated matrix $D^{-1}(k)$

Bl matrix $Bl(k)$

A matrix $A(k)$

ALPHA working storage for $\beta_n$ used in calculating the associated $R_n(k)$

C $\beta_n$, calculated to accuracy of less than 0.005 in magnitude in this study

VEC $R_n(k)$

ORTH the product of $h$ and the summation in the denominator in Equation 25

GANS the product of $h$ and the summation in the second numerator in Equation 27

DNC the product of $h$ and the summation given by Equation 28 for $R_0(k) = 1.0$
ANC the product of h and the summation given by Equation 26 for any \( R_n(k) \)

B \( B_n \)

CC calculated concentrations, used only in checking to determine which concentration distributions could be used to calculate \( p \)

WL large increment used in approximating \( \beta_n \); in this study WL = 0.5

WF small increment used in approximating \( \beta_n \); in this study WF = 0.005

KEV number of eigen values calculated

PI working storage for evaluating the determinant of \((A(k) - \beta I)\) for a previously estimated \( B_n \)

GAM estimated \( \beta_n \)

SEC previously estimated \( \beta_n \)

POL working storage for evaluating the determinant of \((A(k) - \beta I)\) for an estimated \( \beta_n \)

FT storage for any estimated \( \beta_n \)

SAM improved estimate of \( \beta_n \) using small increment WL

V temporary storage for a given \( R_n(k) \)

The FORTRAN statements are listed in sequence in Figure 22.
SOLUTION TO THE STURM-LIOUVILLE PROB. AND ASSOCIATED CALCULATIONS

DIMENSION A(41,41),B(41),C(41),V(41),VEC(41,41),ORTHO(41),CONC(41,110),CANS(41,10),CS(41,41),D(41,41),B1(41,41),R(81),U(81),P(81),
2CC(41,10)

COMMON A,B,C,V,VEC,ORTHO,CONC,CANS,CS,D,B1,R,U,P,ALPHA,DET,N1,N

READ INPUT TAPE 5,4,IDATA,JDATA,KDATA
FORMAT(68H1)
1 GO TO (6,500,501),IDATA
6 READ INPUT TAPE 5,7,V1,V2,V3,NX,MX,F,G,SP,SQ,NN,KP,LV,RINJ
FORMAT(3F10.5,213,2F10.5,2F4.1,310,F7.5)
8 N=(NN+1)/2
81 DO 83 LC=1,LV
82 READ INPUT TAPE 5,83,(COFC(KC,LC),KC=1,N)
83 FORMAT(11F7.4)
9 N1=(NN-1)/2
10 AN=N1
11 H=1./AN
12 R(1)=0.0
13 DO 15 NR=2,NN
14 ANR=NR
15 R(NR)=(H/2.)*(ANR-1.)
161 GO TO (16,19),JDATA
16 DO 17 IT=1,NN
17 U(IT)V1*(1.-R(IT)**NX)+V2*(1.-R(IT)**NX)+V3
18 GO TO 20
19 READ INPUT TAPE 5,191,(U(IS),IS=1,NN)
191 FORMAT(10F8.5)
20 GO TO (21,24),KDATA
21 DO 22 IS=1,NN
22 P(IS)=1.0+F*(R(IS)**SP)+G*(R(IS)**SQ)

Figure 22. FORTRAN statements
23 GO TO 26
24 READ INPUT TAPE 5,25,(P(ISS),ISS=1,NK)
25 FORMAT(10F8.5)
26 DO 29 IR=1,N
27 DO 28 IC=1,N
28 D(IR,IC)=0.0
29 CONTINUE
30 D(1,1)=H*H*0.25*U(2)*R(2)
31 D(N,N)=H*H*0.25*U(NN-1)*R(NN-1)
32 KN=N-1
33 DO 35 IA=2,KN
34 L=2*IA-1
35 D(IA,IA)=H*H*U(L)*R(L)
36 DO 39 IBR=1,N
37 DO 38 IBC=1,N
38 B1(IBR,IBC)=0.0
39 CONTINUE
40 B1(1,1)=P(2)*R(2)
41 B1(1,2)=-P(2)*R(2)
42 DO 47 KR=2,KN
43 11=2*KR-2
44 B1(KR,KR)=P(L1)*R(L1)+P(L1+2)*R(L1+2)
45 B1(KR,KR-1)=-P(L1)*R(L1)
46 B1(KR,KR+1)=-P(L1+2)*R(L1+2)
47 B1(N,N-1)=-P(NN-1)*R(NN-1)
48 B1(N,N)=P(KN-1)*R(NN-1)
49 DO 75 I=1,N
50 D(I,I)=1./D(I,I)
51 DO 76 I=1,N
52 DO 76 J=1,N
53 A(I,J)=0.
54 A(1,1)=D(1,1)*B1(1,1)
55 A(N,N)=D(N,N)*B1(N,N)

Figure 22. (Continued)
DO 80 I=2,KN
K1=I-1
K2=I+1
DO 80 KI=K1,K2
80 A(I,KI)=D(I,1)*B1(I,KI)
A(1,2)=D(1,1)*B1(1,2)
A(N,N-1)=D(N,N)*B1(N,N-1)
NI=1
DETI=100000.0
CALL EIGN
DO 120 I=1,KN
ALPHA=C(1)
CALL VCTR
DO 110 IJ=1,N
110 VEC(IJ,I)=V(IJ)/V(1)
120 CONTINUE
90 DO 91 I=1,KN
91 B(I)=0.0
1203 KF=K-2
1204 DO 1215 IB=1,KN
1201 ABO=0.0
1205 DO 1207 IBO=2,KN
1206 JBO=IBO-1
1207 AND=A0+VEC(IBO,IB)*VEC(IBO,IB)*R(JBO)*U(JBO)
1208 ORTHO(IB)=H*(AND+0.25*U(2)*R(2)*VEC(1,IB)*VEC(1,IB)+0.25*U(N-1)*
1R(NN-1)*VEC(N,IB)*VEC(K,IB))
1209 DO 1214 IBA=1,LV
1202 ANS=0.0
120 DO 1212 IBB=2,KN
1211 IRB=IBB-1
1212 ANS=ANS+CONC(IBB,IBA)*R(IBB)*U(IBB)*VEC(IBB,IB)

Figure 22. (Continued)
CANS(IB,IBA) = H*(ANS+0.25*U(2)*R(2)*VEC(1,IB)*CONC(1,IBA)+0.25*
1U(NN-1)*R(NN-1)*VEC(N,IB)*CONC(N,IBA))

CONTINUE

CONTINUE

DNC=H*(0.25*R(2)*U(2)+RINJ*U(3))
DO 95 NC=1,KP
ANC=H*(0.25*R(2)*U(2)*VEC(1,NC)+RINJ*U(3)*VEC(2,NC))
95 B(NC)=ORTH0(1)*ANC/(ORTHO(NC)*DNC)

DO 1222 LV1=1,LV
DO 1221 NC=1,N
CI=0.0
DO 1220 KP1=1,KP
CI = CI + VEC(NC,KP1)*CANS(KP1,LV1)/ORTHO(KP1)
CC(NC,LV1)=CI
DO 1222

WRITE OUTPUT TAPE 10,4,IDATA,JDATA,KDATA
WRITE OUTPUT TAPE 10,123
FORMAT(37HJ J EIGEN VALUE(J) A(J))
DO 126 JO=1,KP
FORMAT(1H 14,2E18.8)
WRITE OUTPUT TAPE 10,126,JO,C(JO),B(JO)
DO 134 JV=1,KP,5
JC=JV+4
WRITE OUTPUT TAPE 10,130
FORMAT(114HJ I R(I) RVEL(I) PE(I) EIGEN FUNCT(I,1) E F(I,2) E F(I,3) E F(I,4) E F(I,5))
DO 132 IV=1,NN
IV=(IW+1)/2
WRITE OUTPUT TAPE 10,133,IW,R(IW),U(IW),P(IW),(VEC(IW,JT),JT=JV,JC 1)
FORMAT(1H I3,3F9.5,5E17.8)
CONTINUE
DO 147 KJ=1,LV,5
KF=KJ+4

Figure 22. (Continued)
Figure 22. (Continued)
DO 699 I=1,KEV
630 DO 657 J=1,999
SJ=J
GAk=FA+SJ*WL
SEC=GAk
B(1)=A(1,1)-GAm
B(2)=(A(2,2)-GAm)*B(1)-A(1,2)*A(2,1)
650 DO 651 K=3,N
651 B(K)=(A(K,K)-GAl)*B(K-1)-A(K-1,K)*B(K-2)
652 POL=B(N)
653 IF(POL)655,671,654
654 IF(P1)658,656,656
655 IF(P1)656,656,658
656 P1=B(N)
656 FT=GAk
657 CONTINUE
658 DO 670 L=1,999
SAk=FT+WF
SEC=SAk
660 B(1)=A(1,1)-SAM
661 B(2)=(A(2,2)-SAh)*B(1)-A(1,2)*A(2,1)
662 DO 663 KF=3,N
663 B(KF)=(A(KF,KF)-SK)*B(KF-1)-A(KF-1,KF)*B(KF-2)
664 POL=B(N)
665 IF(POL)667,681,666
666 IF(P1)672,669,669
667 IF(P1)669,669,669
669 FT=SAk
670 P1=B(N)
671 C(I)=GAl
672 FA=GAh
673 P1=B(N)
   GO TO 699
681 C(I)=SAh

Figure 22. (Continued)
SUBROUTINE VCTR

DIMENSION A(41,41), B(41), C(41), V(41), VEC(41,41), ORTHO(41), CO (:C(41,110), CANS(41,10), CS(41,41), E(41,41), BI(41,41), R(41), U(41), P(41),
EC(41,10),

513 V(1)= 1.0
514 V(2)=-1.*((A(1,1)-ALPHA)*V(1)/A(1,2)
515 DO 516 JV= 3, N
516 V(JV)=-1.*((A(JV-1,JV-2)*V(JV-2)+(A(JV-1,JV-1)-ALPHA)*V(JV-1))
1A(JV-1,JV)
RETURN
END

Figure 22. (Continued)