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Laminar Dispersion in Capillaries:

Part I. Mathematical Analysis

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Since 1953, when G. I. Taylor first considered the problem, numerous studies of the miscible displacement of fluids in capillaries have produced several approximate mathematical solutions which are purported to be valid under different conditions. Their form and ranges of applicability have been in conflict to some extent, since no exact solution is available to check these expressions.

This study has resulted in exact numerical solutions to this problem with both axial and radial molecular diffusion accounted for. The range of parameters investigated is wide enough for comparison with all known analytical and empirical results and covers τ from 0.01 to 30 and N_{Pe} from 1 to 23,000. It is shown that for sufficiently large values of τ the Taylor-Aris theory is valid and thus results for all τ and N_{Pe} of any practical interest are now known.

Axial molecular diffusion is significant at lower values of the Peclet number but the magnitude of N_{Pe} at which this occurs depends on the value of τ. In general, axial molecular diffusion is important for Peclet numbers less than about 100.

Present results show that there is no justification for Bailey and Gogarty's empirical modification which yields an exponent of 0.541 rather than 0.50 for τ in Equations (35) and (36). Also, for the system studied here, no justification was found for the conjecture of Bournia et al. that Aris' low N_{Pe} modification may not account for axial diffusion properly.

Simple expressions given by Equations (48) and (50) were developed empirically and they give with good accuracy the average concentration distribution over wider ranges of N_{Pe} and τ than previously reported expressions.

In 1953, G. I. Taylor (*11* to *13*) discussed the rather complex problem of aperiodic dispersion in tubes that occurs when a solute is transported by a stream of nonuniform velocity; since that time this problem has received a considerable amount of attention from other investigators. Aris (*1, 2*) extended Taylor's work by using the method of moments, which is an interesting integral type of approach to the problem. Van Deemter et al. (*7*) also employed an integral method and discussed their results in terms of Danckwerts' holdback concept.

More recently, Bailey and Gogarty (*3*) employed an unorthodox numerical method to solve the convection equation with axial molecular diffusion ignored, which, in effect, limits the solution to large Peclet numbers. They used the pure convection solution for short values of time and then continued the solution by a technique such that the convection term was accounted for by moving the solutions down the flow. This approach essentially accounts for radial diffusion and axial convection alternately rather than simultaneously. Also, Phillip (*10*) studied the periodic dispersal problem by using eigenfunction expansions and discussed the applicability of the diffusion model to dispersion systems of this type.

Experimental results for dispersion in tubes have been reported by a number of investigators (*3* to *5, 11*). For large Peclet numbers these results are in rather good agreement with each other, and for reasonably large values of time all of them agree with Taylor's approximate solutions. However, for slow flows the effect of Peclet number has not been determined yet satisfactorily and the limits of applicability of the Taylor-Aris solution are in doubt. Also, at low velocities, experimental results of Bournia et al. (*5*) yield values of the dispersion coefficient k which are far greater than those predicted by Bailey and Gogarty (*3*) and Taylor (*11*). Furthermore, there is a dearth of information regarding point concentration distribution, which is needed to gain a better understanding of the dispersion process.

Dispersion problems have considerable practical importance in a variety of fields. Taylor originally attacked the problem by stating that it described the dispersion of soluble materials in blood vessels. Phillip said that the dispersal of solutes in water conducting organs of plants follows similar laws. Van Deemter et al. (*7*) and Golay (*8*) pointed out the use of such theories in describing chromatographic columns. Westhaver (*15*) and Aris (*2*) discussed applications to distillation processes. We are interested because of the connection of this problem with the batch washing of ice particles to free them of brine before melting.

In the present work we solve the diffusion-convection equation including the axial diffusion term numerically and our purposes are to:

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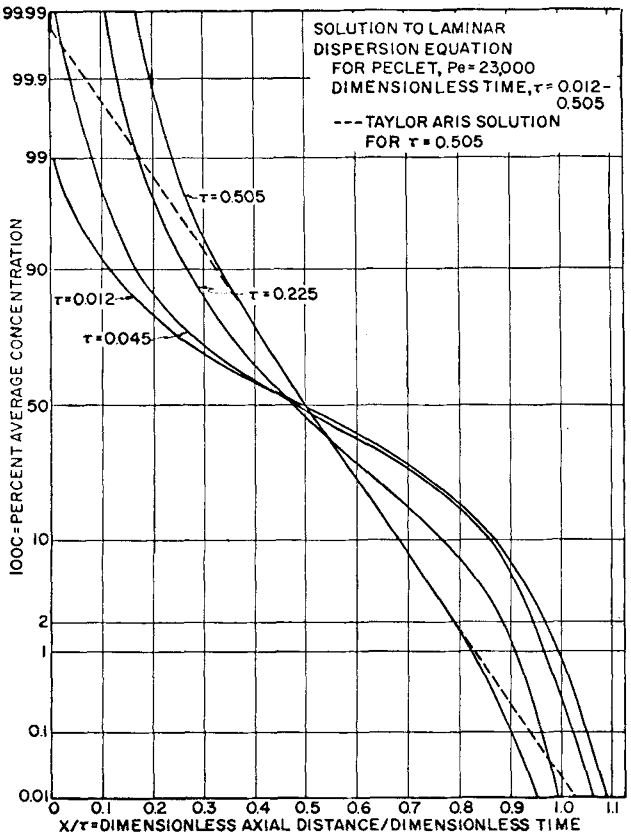

Fig. 1a. Numerical results for Peclet number = 23,000.

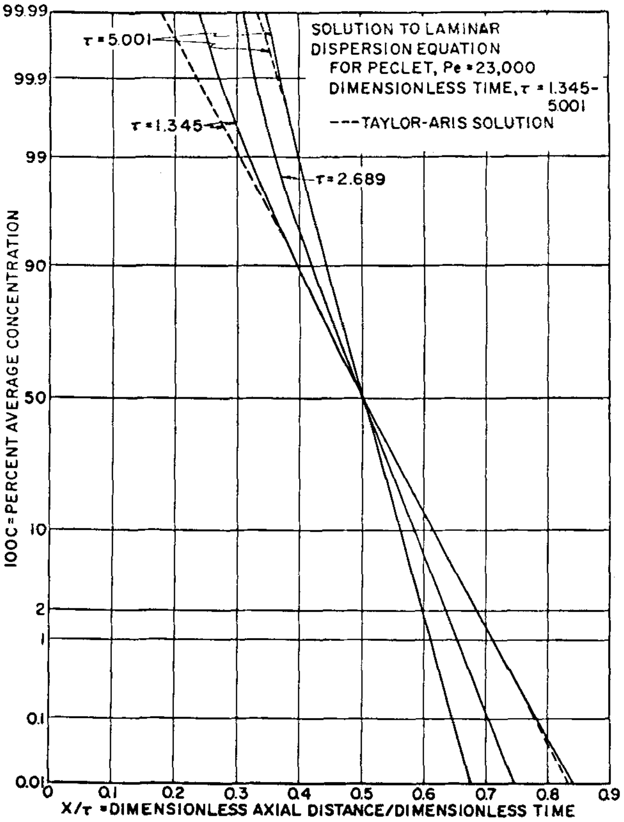

Fig. 1b. Numerical results for Peclet number = 23,000.

1. Provide detailed information on the dispersion process in tubes in terms of point, average, and bulk concentration distributions.
2. Delineate the role of axial molecular diffusion characterized by the Peclet number, in well-defined dispersion systems.
3. Check the numerical solutions obtained for high Peclet number systems by Bailey and Gogarty, since their solution seemed unreasonable in that the argument of the complementary error function contained the dimensionless time to the 0.541 power [see Equations (35) and (36)]. If Taylor's solution is truly the limiting case for high N_{Pe} and τ as Aris' analysis indicates, then this exponent must approach 0.5 and any other value is unsafe for extrapolation.
4. Check the conjecture of Bournia et al. that Aris' result may not account properly for axial molecular diffusion at low Peclet numbers.
5. Develop simple expressions to describe dispersion systems in regions where the Taylor-Aris theory is not applicable.

MATHEMATICAL ANALYSIS

For fully developed laminar tube flow, the convection equation describing the concentration C^+ of solute material as a function of the axial distance x, the radial distance r, and time t, is given by the partial differential equation

$$D\left(\frac{\partial^2 C^+}{\partial x^2}+\frac{\partial^2 C^+}{\partial r^2}+\frac{1}{r}\frac{\partial C^+}{\partial r}\right)=\frac{\partial C^+}{\partial t}+u_o\left(1-\frac{r^2}{a^2}\right)\frac{\partial C^+}{\partial x} \quad (1)$$

and for the aperiodic system considered here, the boundary conditions are

$$\begin{aligned} C^+(0,x,r)&=0 \quad x>0\\ C^+(t,0,r)&=C_o^+ \quad t\geqq 0\\ C^+(t,\infty,r)&=0\end{aligned} \quad (2)$$

$$\frac{\partial C^+}{\partial r}(t,x,0)=\frac{\partial C^+}{\partial r}(t,x,a)=0$$

To make this system of equations dimensionless, we make the following transformations:

$$X=\frac{xD}{a^2u_o},\ \tau=\frac{Dt}{a^2},\ \eta=\frac{x}{au_o}\sqrt{\frac{D}{t}}=\frac{X}{\sqrt{\tau}},\ C=\frac{C^+}{C_o^+},\ y=\frac{r}{a}$$

where the transformation $\eta=\dfrac{X}{\sqrt{\tau}}$ is suggested by the analytical solution to the pure diffusion problem.

After we introduce these transformations, Equations (1) and (2) become

$$\frac{\partial C}{\partial \tau}+\left[\frac{(1-y^2)}{\sqrt{\tau}}-\frac{1}{2}\frac{\eta}{\tau}\right]\frac{\partial C}{\partial \eta}=\frac{\partial^2 C}{\partial y^2}+\frac{1}{y}\frac{\partial C}{\partial y}+\frac{1}{\tau N^2_{Pe}}\frac{\partial^2 C}{\partial \eta^2} \quad (3)$$

with the conditions

$$\begin{aligned} C(0,\eta,y)&=0 \quad \eta>0\\ C(\tau,0,y)&=1 \quad \tau\geqq 0\\ C(\tau,\infty,y)&=0\end{aligned} \quad (4)$$

$$\frac{\partial C}{\partial y}(\tau,\eta,0)=\frac{\partial C}{\partial y}(\tau,\eta,1)=0$$

In the formulation given above a step change is used to describe the inlet condition to the capillary. This con-

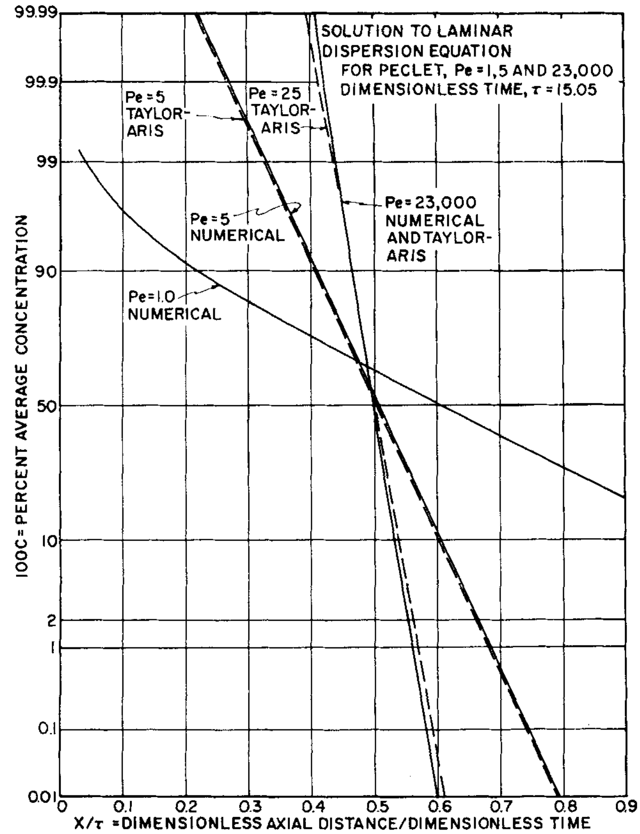

Fig. 1c. Numerical results for Peclet number = 1, 5, and 23,000 at τ = 15.05.

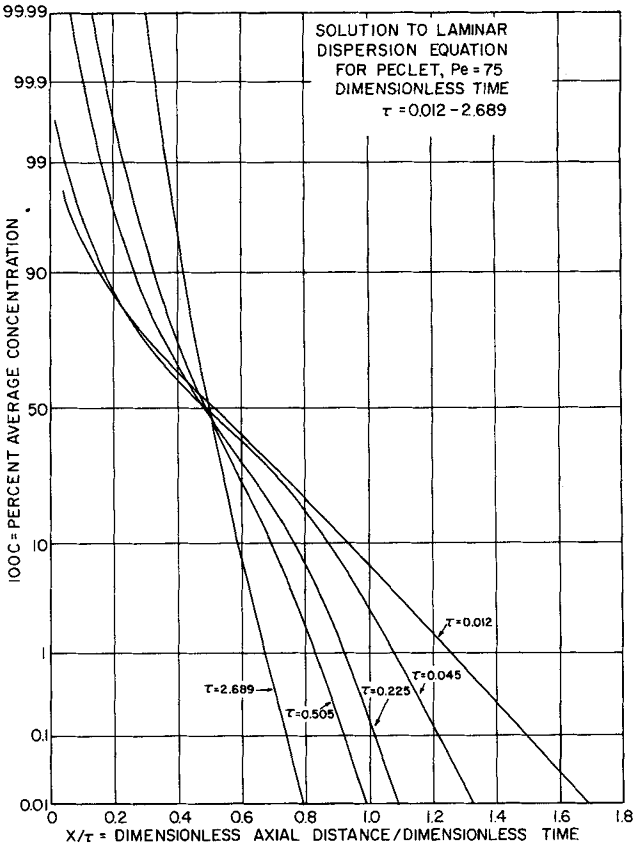

Fig. 2. Numercial results for Peclet number = 75.

dition describes the situation when the capillary is fed from a well-mixed reservoir of uniform concentration C_o^+. Other inlet boundary conditions, such as that proposed by Danckwerts, can also be employed and the appropriateness of these conditions depends on the physical problem under consideration. In a later paper it will be shown that the same asymptotic solution for large τ is obtained independent of the inlet condition if it is aperiodic.

The use of finite-difference formulas for solving Equations (3) and (4) is not a particularly straightforward method, since stability and convergence of these approaches must be determined more or less by trial and error. Furthermore, there is a tendency for the initial discontinuity to propagate along the flow and it is necessary that errors such as this attenuate and become negligible as the solution is continued in order for one to be sure that the numerical results are valid. This difficulty is particularly troublesome for large Peclet numbers, since here convection dominates at small values of time. With small Peclet numbers, axial molecular diffusion is a particularly important factor at small values of time and tends to eliminate the discontinuity quickly.

The finite-difference method used here is based on those proposed by Peaceman and Rachford (*20*) and also by Douglas (*9*), wherein an alternating direction implicit procedure was presented. This method requires the line-by-line solution of small sets of simultaneous equations that can be solved by a direct, noniterative method. Peaceman and Rachford analyzed this procedure for simple two-dimensional problems and showed it to be unconditionally stable for any size time step and to require much less work than other methods studied. However, in the present dispersion problem, since the governing equations are more complex, it is very difficult to analyze the convergence and stability without actual computations. Hence, the size of the η, y, and τ increments for this study are determined mainly by trial and error.

Without going into the details of the modified Peaceman and Rachford method used here for solving the dispersion problem, we describe briefly the general numerical technique and the application of the method as follows.*

The cylindrical tube is divided into a series of blocks, each of length $\Delta\eta$ and of width Δy. At each location, the convection equation is represented by the corresponding difference equation, which is implicit alternately with respect to y and η for successive time steps. For each τ value, the finite-difference representation results in as many simultaneous equations as the number of η or y steps. When we solve these equations simultaneously by using Thomas' method (*14*), the concentration distribution for all the points in the tube is obtained for a particular value of τ. These point concentrations then are used to compute the average and bulk concentrations. The above procedure is repeated until the desired value of τ is reached.

DISCUSSION OF RESULTS

Solutions have been obtained for ten different Peclet numbers: 23,000, 2,000, 500, 100, 75, 50, 25, 10, 5, and 1.† These results will be discussed in two categories: high

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*The details of the mathematical analysis, which includes Equations (5) through (32), have been deposited as document 8544 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $7.50 for photoprints or $2.75 for 35-mm. microfilm.

†A summary of the conditions for which numerical results were obtained and tabulations of the average and bulk concentration distributions for the entire range of τ and N_{Pe} investigated are also available from the American Documentation Institute.

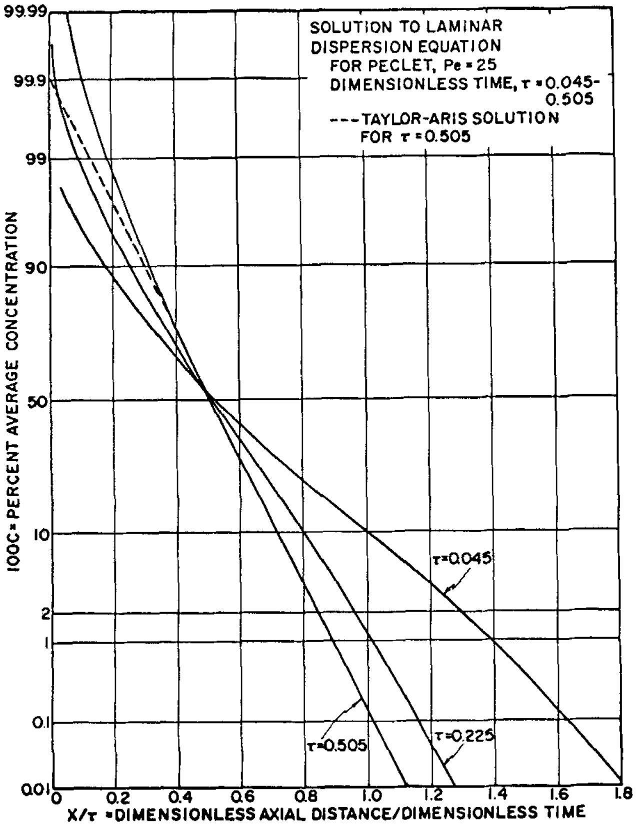

Fig. 3a. Numerical results for Peclet number = 25.

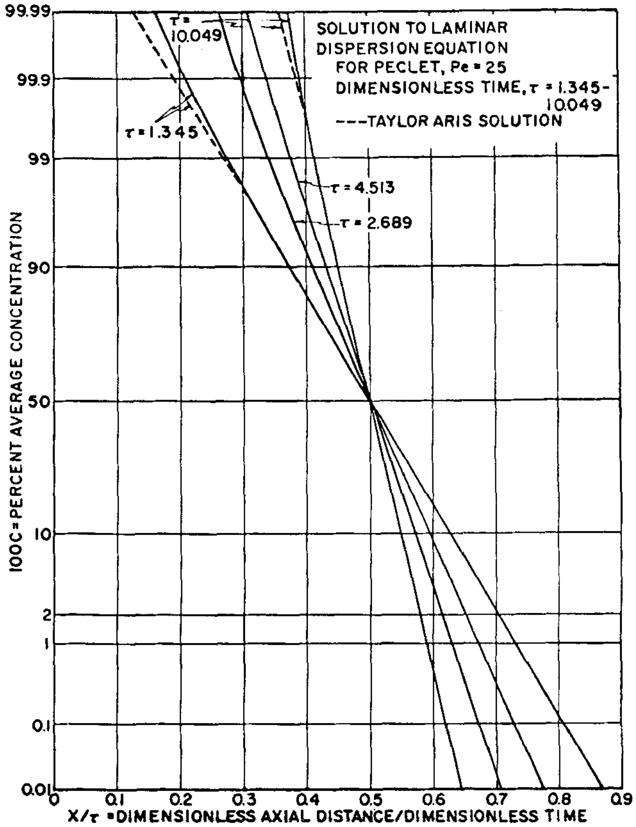

Fig. 3b. Numerical results for Peclet number = 25.

Peclet number results and low Peclet number results. This division is based on whether or not the effect of axial molecular diffusion is significant. In many of these cases solutions have been obtained for τ ranges from as low as 0.01 to as high a value as 30.00.

High Peclet Number Results

The results for high Peclet numbers, 23,000, etc., were found to check very well with the already published (*11*) approximate analytical and experimental results when $\tau \geqq 0.8$. The solutions for these values and any Peclet numbers above 500 are identical for all practical purposes and thus represent the case where axial molecular diffusion is negligible. Even at a Peclet number of 100 the solutions deviate from very high Peclet number results only for τ values less than 0.225.

Numerical solutions for the high Peclet number ranges are seen in Figures 1*a*, 1*b*, and 1*c* as plots of the normalized concentration C_{avg} vs. axial distance X/τ, for various values of dimensionless time τ. Taylor has given experimental data for three different times—τ = 0.045, 0.135, 2.689—at high Peclet number. Our numerical solution agrees very well with all three.

If the data were plotted on a linear scale, it could be seen that at very low τ values, say 0.012, the plot is a straight line and coincides with the pure convection solution:

$$C_{\text{avg}} = 1 - \frac{X}{\tau}\left(0 < \frac{X}{\tau} < 1\right) \qquad (33)$$
$$= 0 \quad \left(\frac{X}{\tau} > 1\right)$$

In other words, at small times both axial and radial diffusion are negligibly small compared to the convective effects involved. As τ increases, the effect of radial diffusion becomes more important and the curves become symmetrical with respect to the pure convection solution. At sufficiently large τ ($\tau > 0.8$) they become error functions, as can be seen by their linearity on a probability graph, as in Figure 1*b*.

Taylor has given an approximate analytical solution of Equations (3) and (4) as

$$C_{\text{avg}} = 0.5 \text{ erfc}\left(\frac{1}{2} x_1 k^{-1/2} t^{-1/2}\right) \qquad (34)$$

where

$$x_1 = x - \frac{1}{2} u_o t$$

and

$$k = \frac{a^2 u_o^2}{192D}$$

By transforming this into the dimensionless variables defined previously, we get

$$C_{\text{avg}} = 0.5 \text{ erfc} \frac{(X - \tau/2)}{\sqrt{\tau/48}} \qquad (35)$$

Bailey and Gogarty also suggested from their numerical results that for $0.5 < \tau < 6.0$

$$C_{\text{avg}} = 0.5 \text{ erfc} \frac{X - \tau/2}{(\tau)^{0.541}/\sqrt{48}} \qquad (36)$$

Present numerical results for $\tau > 0.8$ are essentially error functions and correspond to Equation (35) more closely than to Equation (36). Figure 1*b* illustrates the agreement between Equation (35) and the finite-difference solutions.

The behavior mentioned above can be seen also by examining the dimensionless mixing zone length L, defined by Taylor as the distance from the 10 to the 90% points on the C_{avg} curve. Values of L obtained numerically are plotted in Figure 7 as a function of τ. This plot resembles

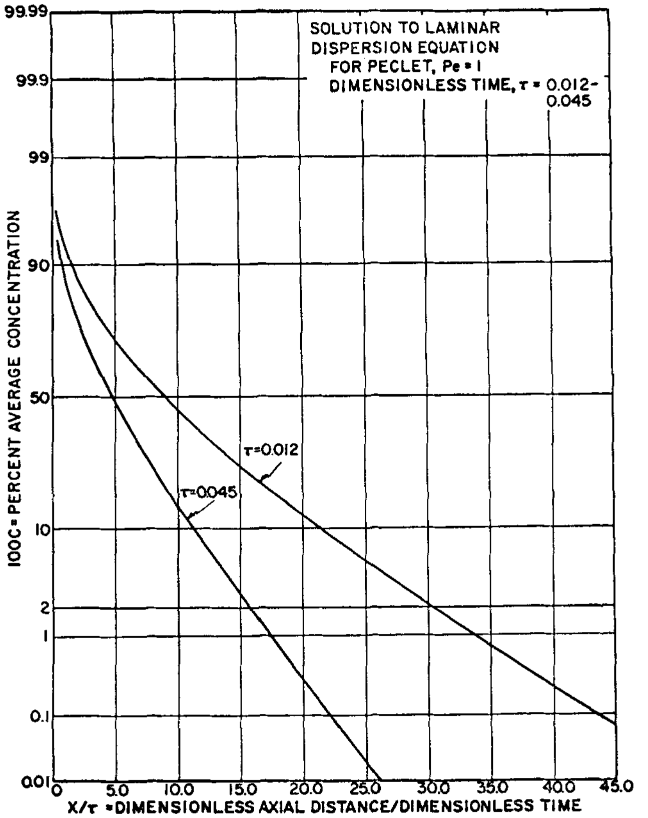

Fig. 4a. Numerical results for Peclet number = 1.

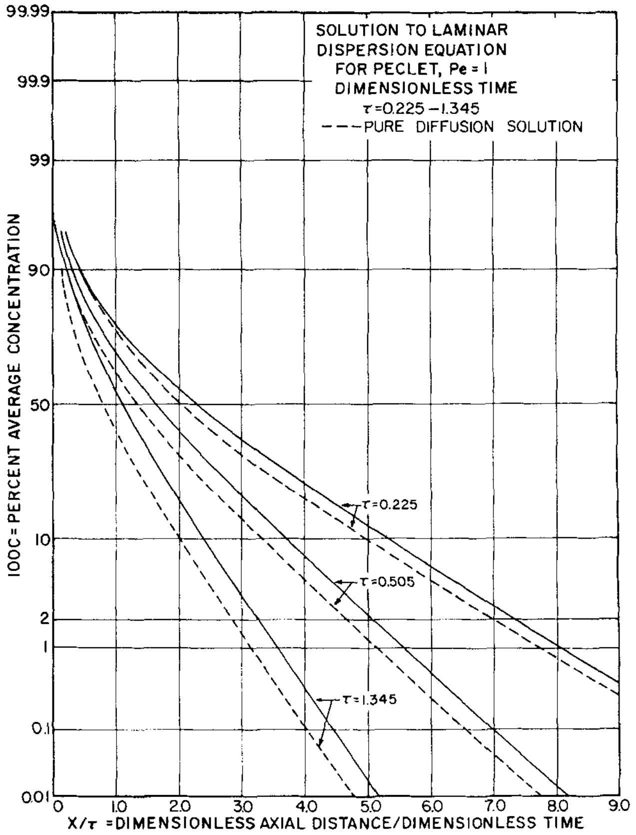

Fig. 4b. Numerical results for Peclet number = 1.

the one given by Bailey and Gogarty but the equation describing the curve above the break point (region 2, reference 3) is found to be $L = 0.26\ \tau^{0.50}$. Hence our numerical solutions for high Peclet numbers substantiate Taylor's theory for sufficiently large values of τ and do not corroborate the empirical modification of the exponent of τ suggested by Bailey and Gogarty.

Low Peclet Number Results

As the Peclet number decreases, axial molecular diffusion becomes significant, but the magnitude of the Peclet number at which this occurs and how this magnitude is influenced by τ were not known. Thus the low Peclet number region was investigated thoroughly in this study. A reasonable idea of the effect of axial diffusion is given by Figure 1*c*. The figure shows that, for large τ and a Peclet number of 25, the deviations and hence the effect of axial diffusion are comparatively small. However, the calculations show that the effect of axial diffusion becomes significant for Peclet numbers less than 500, but this effect is important only for very short times at $N_{Pe} > 100$ as will be discussed later in conjunction with Figure 8.

The effect of axial diffusion can be noticed clearly from Figures 3*a* and 4*a* through *d** in that the solute is present far beyond the $X/\tau = 1$ point on the abscissa. The significance of the location $X/\tau = 1$ is that this is the location of the tip of the parabolic front of the velocity distribution. At large Peclet numbers the solvent-solution interface is diffuse and centered about $X/\tau = 1/2$. Dispersion by pure convection yields solute up to but not beyond $X/\tau = 1$ and rapid radial diffusion tends to eliminate solute from this region (when solution is injected into solvent) and to keep it back near $X/\tau = 1/2$. The existence of solute beyond $X/\tau = 1$ thus can occur only by axial molecular diffusion.

In all cases, including those of large N_{Pe}, axial molecular diffusion predominates over axial convection if τ is sufficiently small. At larger values of N_{Pe} this is of limited practical significance because τ must be so small. However, if N_{Pe} is small enough then the pure diffusion region can extend to large values of τ.

As the Peclet number decreases from 100 to 1.0, the importance of axial diffusion increases correspondingly until a stage is reached at very low Peclet numbers when, for most practical purposes, the dispersion takes place essentially by diffusion only, as in Figures 4*a* and 4*b*. In fact, at a Peclet number of 1.0 the solute is found to have dispersed to $X/\tau = 50$ at $\tau = 0.012$, as seen in Figure 4*a*. In other words, molecular diffusion has moved the material out fifty times as far as the convection. Thus it seems desirable to define limits for the pure diffusion region in terms of τ and N_{Pe}, and an approximate relation describing the range of τ in which dispersion takes place primarily by molecular diffusion is developed here. The criterion used to determine this range depends on the ratio of the pure convective length X_{conv} to the pure diffusive length X_{diff}, which is given by

$$(X_{\text{conv}}/X_{\text{diff}}) \propto N_{Pe}\sqrt{\tau}$$

Hence for pure diffusion to occur, the quantity $N_{Pe}\sqrt{\tau}$ must be less than some number A. The value of A is determined by plotting the Peclet number vs. the value of τ below which the pure diffusion solution holds.

It was found that this plot is linear on logarithmic scales and from the slope and the intercept it is found that the maximum value of A up to which pure diffusion predominates is equal to approximately 0.5. The general requirement for the pure diffusion equation to hold can be written as

$$N_{Pe}\sqrt{\tau} < 0.5 \qquad (37)$$

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*Several additional figures of plotted data are available elsewhere. See footnote on page 1065.

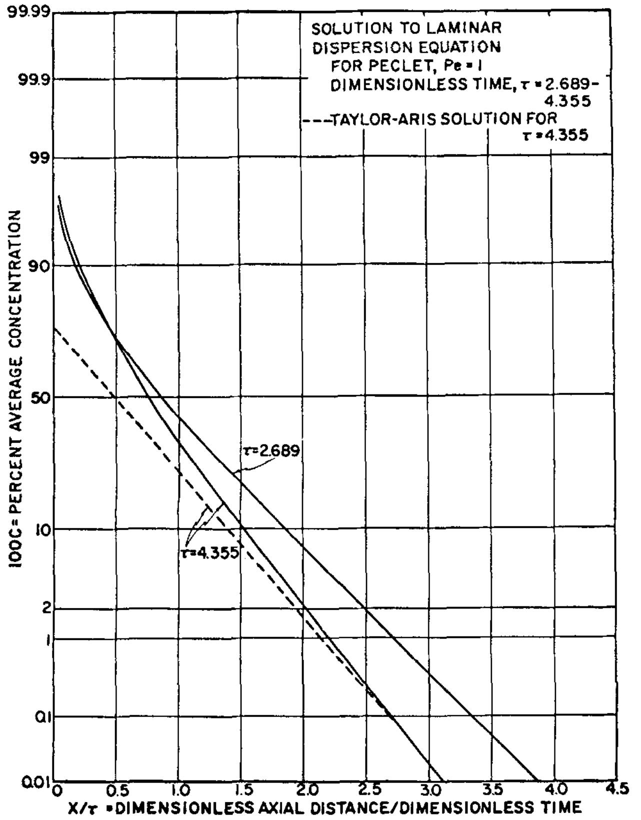

Fig. 4c. Numerical results for Peclet number = 1.

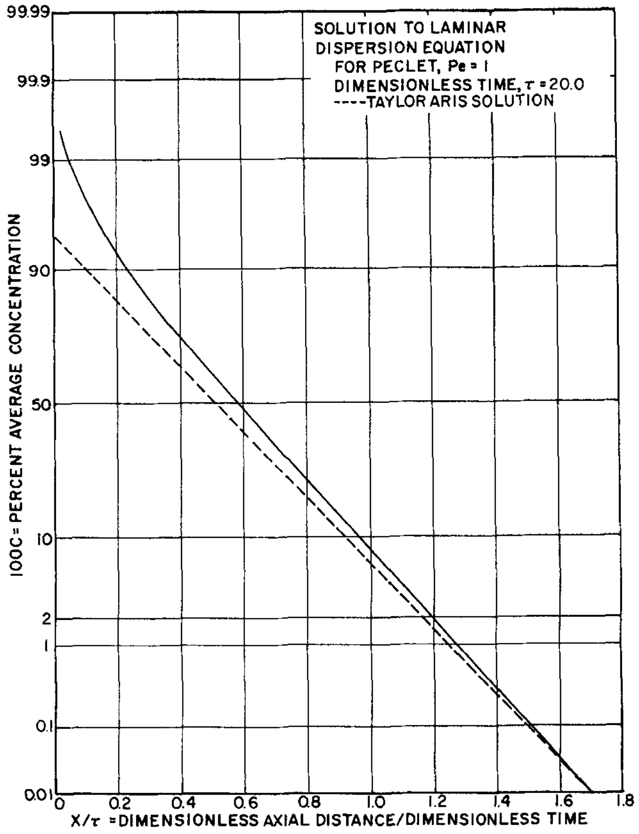

Fig. 4d. Numerical results for Peclet number = 1.

As in the case of high Peclet numbers, the solutions become linear on a probability plot for high τ values. It can be seen from Figures 3*b*, 4*c*, and 4*d* that the higher the Peclet number, the faster the solution tends to be an error function curve. A region of practical importance has been studied by Aris (*1*), who concluded that in cases where axial molecular diffusion was significant, Taylor's approximate solution can be modified by replacing the dispersion coefficient k by $K = k + D$. The result then can be written for low Peclet numbers as

$$C_{avg} = \frac{1}{2} \operatorname{erfc} \left[\frac{1}{2} x_1 (k + D)^{-1/2} t^{-1/2} \right] \tag{38}$$

or in dimensionless form as

$$C_{avg} = \frac{1}{2} \operatorname{erfc} \frac{(X - \tau/2)}{\left[\frac{\tau}{48} + \frac{4\tau}{N^2_{Pe}} \right]^{0.5}} \tag{39}$$

where the term $4\tau/N^2_{Pe}$ in the denominator accounts for axial diffusion. Figures 1*b*, 1*c*, and 3*b* show that the numerical solutions obtained correspond very well with Equation (39) as long as τ exceeds the minima shown in Table 1. The criterion used to find the minimum values of τ in Table 1 was rather subjective; the values were so chosen that at a C of 99.5% the two values of X/τ agreed within 0.01 to 0.05.

TABLE 1. APPROXIMATE τ VALUES ABOVE WHICH SOLUTION FOLLOWS TAYLOR-ARIS SOLUTION

Peclet number	Minimum τ
>500	0.80
100	0.80
50	1.10
25	1.25
10	1.75
5	4.50
1	>20.00

Frequently, at regular time intervals values of point concentration were printed out in addition to the average and bulk concentrations to gather information about radial concentration distributions. Typical radial profiles are shown in Figure 5. An approximate equation for point concentration distributions has been given by Taylor as

$$C = C_{avg} + \frac{a^2U}{4D} \frac{\partial C_{avg}}{\partial x_1} \left(-\frac{1}{3} + y^2 - \frac{1}{2} y^4 \right) \tag{40}$$

where C_{avg} is given by Equation (39) By substituting this value in Equation (40) and making the equation dimensionless, we get

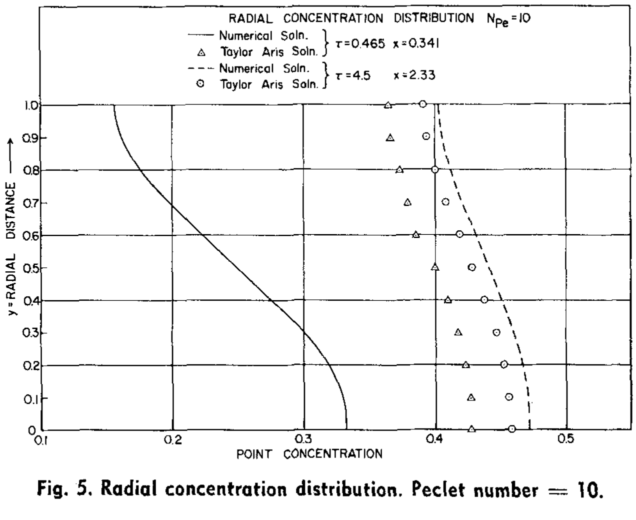

Fig. 5. Radial concentration distribution. Peclet number = 10.

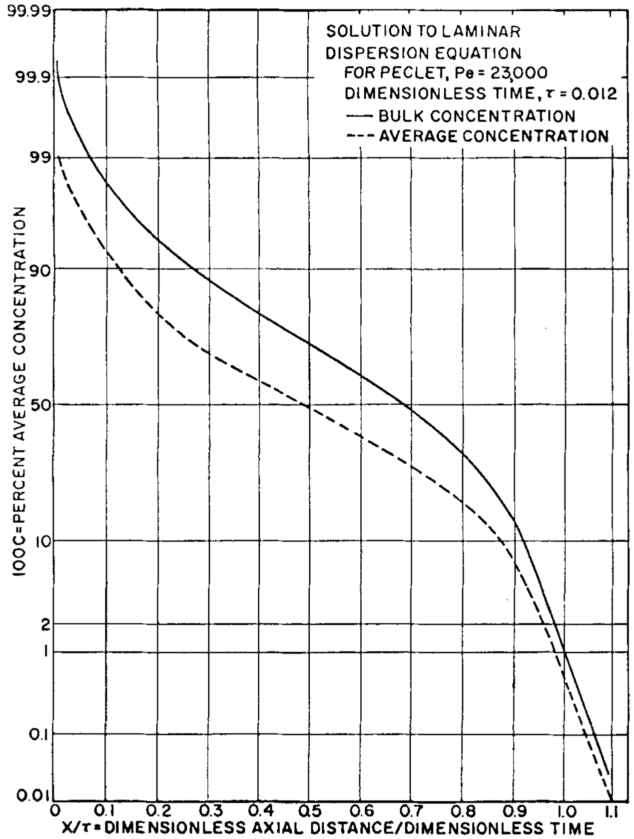

Fig. 6a. Comparison between average and bulk concentration. Peclet number = 23,000.

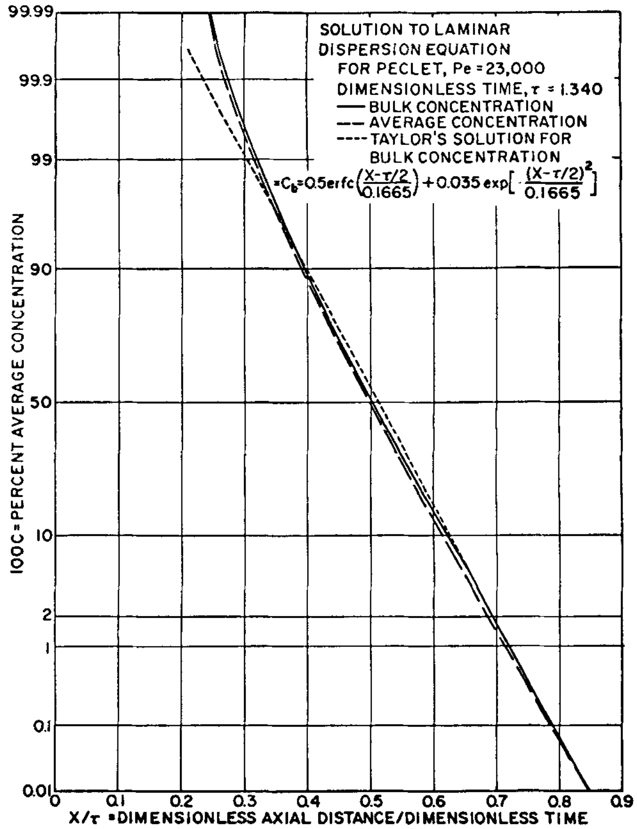

Fig. 6b. Average and bulk concentrations. Peclet number = 23,000.

$$C = 0.5 \operatorname{erfc} \frac{(X - \tau/2)}{\sqrt{K_1}} - \frac{1}{8\sqrt{K_1 \pi}} \exp \left[- \frac{(X - \tau/2)^2}{K_1} \right] \left(- \frac{1}{3} + y^2 - \frac{1}{2} y^4 \right) \tag{41}$$

where

$$K_1 = \frac{\tau}{48} + \frac{4\tau}{N^2_{Pe}} \tag{42}$$

In Figure 5 the numerical solution is compared with the solution obtained from Equation (41), which shows two cases, in one of which the agreement is poor. It was found that for $N_{Pe} \geqq 25$ the two solutions for point distributions agree well in all cases where τ is sufficiently large for the Taylor-Aris solution to be valid for C_{avg}. Thus the criteria for agreement are substantially the same as given in Table 1. For very low Peclet numbers, say $N_{Pe} \leqq 10$, it appears that somewhat larger values of τ than those shown in Table 1 are required to obtain agreement comparable to that obtained in the case of large N_{Pe}. This can be seen in Figure 5 where $\tau = 4.50$ there is still an average difference of about 2.5% between the two solutions for the point concentration distribution.

A knowledge of the relationship between C_{bulk} and C_{avg} may be very useful to formulate a general solution for the concentration distribution especially at the lower time values where C_{bulk} is different from C_{avg}. Therefore, Figures 6*a* and 6*b* show a comparison of the average and the bulk concentration distributions for a Peclet number of 23,000. It can be clearly seen from these plots that as the value of τ increases, the average and bulk concentration distributions tend to become identical and at lower times they differ significantly from each other. This was true for low Peclet numbers also.

An approximate solution for C_{bulk} can be obtained from Equation (41) as

$$C_{\text{bulk}} = 0.5 \operatorname{erfc} \frac{(X - \tau/2)}{\sqrt{K_1}} + \frac{1}{96\sqrt{K_1 \pi}} \exp \left[- \frac{(X - \tau/2)^2}{K_1} \right] \tag{43}$$

For the bulk concentration Equation (43) is found to be satisfactory for high τ values where C_{bulk} is approximately equal to C_{avg} as indicated by Figure 6*b*. But for low values of τ, this equation does not agree with the numerical solution.

It can be seen from the discussion on high and low Peclet numbers, that the Taylor-Aris approximate analytical solution does not predict successfully the concentration distribution at τ values below the minima given in Table 1. Hence, a more general solution for the concentration distribution is desirable and is obtained below.

Equation (1) when transformed into the dimensionless form without introducing the η coordinate gives

$$\frac{\partial C}{\partial \tau} + (1 - y^2) \frac{\partial C}{\partial X} = \frac{\partial^2 C}{\partial y^2} + \frac{1}{y} \frac{\partial C}{\partial y} + \frac{1}{N^2_{Pe}} \frac{\partial^2 C}{\partial X^2} \tag{44}$$

with the conditions

$$\begin{aligned} &C\,(0, X, y) = 0 \quad X > 0 \\ &C\,(\tau, 0, y) = 1 \quad \tau \geqq 0 \\ &C\,(\tau, \infty, y) = 0 \end{aligned} \tag{45}$$

$$\frac{\partial C}{\partial y}\,(\tau, X, 0) = \frac{\partial C}{\partial y}\,(\tau, X, 1) = 0$$

Equation (44) when multiplied by y and integrated from 0 to 1 with respect to y becomes

$$\frac{\partial C_{\text{avg}}}{\partial \tau} + \frac{1}{2} \frac{\partial C_{\text{bulk}}}{\partial X} = \frac{1}{N^2_{Pe}} \frac{\partial^2 C_{\text{avg}}}{\partial X^2} \tag{46}$$

Now, from the definition of bulk concentration given by Equation (32) one gets

$$C_{\text{bulk}} = 2\,C_{\text{avg}} - 4\int_0^1 y^3 C\,dy$$

and by using the dimensionless form of Equation (40) and by substituting in Equation (46), one gets

$$\frac{\partial C_{\text{avg}}}{\partial \tau} + \frac{1}{2}\,\frac{\partial C_{\text{avg}}}{\partial X} - P\,\frac{\partial^2 C_{\text{avg}}}{\partial X^2} = -\frac{1}{96}\,\frac{\partial^2 C_{\text{avg}}}{\partial X \partial \tau} \tag{47}$$

where

$$P = \frac{1}{N^2_{Pe}} + \frac{1}{192}$$

Following Taylor, we assume first that the term on the right-hand side of Equation (47) is negligible. Then the solution to the resulting equation which satisfies

$$C_{\text{avg}}(0, X) = 0,\ C_{\text{avg}}(\tau, 0) = 1$$

is well known to be

$$C_{\text{avg}} = \frac{1}{2}\left[\operatorname{erfc}\frac{(X - \tau/2)}{2\sqrt{P\tau}} + \exp\left[\frac{X}{2P}\right]\operatorname{erfc}\frac{(X + \tau/2)}{2\sqrt{P\tau}}\right] \tag{48}$$

If Equations (39) and (48) are compared it is clear that an additional term involving the product of an exponential and complementary error function is obtained. Equation (48) is found to agree very well with the numerical results for all Peclet numbers for values of τ somewhat smaller than those given in Table 1 and becomes identical to the Taylor-Aris result for τ sufficiently large. Furthermore, at very low Peclet numbers, $1/N^2_{Pe} >> 1/192$ and therefore $P = 1/N^2_{Pe}$. With this value of P, Equation (48) predicts the average concentration for all cases where the pure diffusion solution

$$C_{\text{avg}} = \operatorname{erfc}\left[\frac{X N_{Pe}}{2\sqrt{\tau}}\right] = \operatorname{erfc}\left[\frac{x}{2\sqrt{Dt}}\right] \tag{49}$$

applies, since Equation (48) reduces immediately to Equation (49) as $N_{Pe} \to 0$.

Hence, Equation (48), with

$$P = \frac{1}{N^2_{Pe}} + Q$$

predicts the C_{avg} very well for all Peclet numbers in the following τ ranges: for all τ above the minima given in Table 1, when $Q = 1/192$; and for all τ below the value obtained from Equation (37), when $Q = 0$. Consequently, one might hope that Equation (48) could be altered to predict the concentration distribution for all Peclet numbers for τ values in range lying between these two ranges simply by varying the value of Q from 0 to 1/192.

To find a general relation which enables one to use an appropriate value of Q, the following procedure was adopted. First, the C_{avg} curves obtained numerically were fitted by Equation (48) with the appropriate values of Q obtained by trial and error. These Q values were then plotted against τ for the different Peclet numbers. It was then observed that the Q vs. τ relationship was essentially linear on a log-log plot and the same for all Peclet numbers. Hence, Q is independent of the Peclet number and is given by the relationship

$$\begin{aligned} Q &= 0.007\,\tau^{0.55} && \tau < 0.6 \\ Q &= \frac{1}{192} && \tau > 0.6 \\ Q &= 0 && N_{Pe}\sqrt{\tau} < 0.5 \end{aligned} \tag{50}$$

Equation (48) with (50) is then an approximate solution of Equation (47) and it is found that it predicts the C_{avg} distribution throughout the entire range of Peclet number and τ values accurately, as long as the Peclet number $\lesssim 25$. When $N_{Pe} > 25$, the percentage error of the calculated vs. the numerical value increases as τ decreases from 0.6 to 0.1. Hence, for high Peclet numbers and for τ values less than 0.6, Equation (48) does not describe the C_{avg} distribution accurately.

It then seems that in these particular cases the right-hand side of Equation (47) may be important and hence cannot be neglected. To test this, one can solve Equation (47) in a straightforward manner by using the Laplace transform method with the result that

$$C_{\text{avg}} = e^{-96X} + 136e^{-96X}\,X\int_0^\tau \left\{ e^{-144\lambda}\,\frac{[I_1(136\sqrt{\lambda^2 + 2X\lambda}]}{\sqrt{\lambda^2 + 2X\lambda}} \right\} d\lambda \tag{51}$$

However, it can be easily shown that Equation (51) does not satisfy the initial condition which was included formally in the method; consequently we have a contradiction. Apparently, this is caused by the fact that Equation (47), with the inclusion of the $\dfrac{\partial^2 C}{\partial X \partial \tau}$ term, becomes a hyperbolic partial differential equation which is incompatible with the given initial and boundary conditions, and the problem appears to be ill posed. Thus, it seems necessary as well as convenient to neglect $\dfrac{\partial^2 C}{\partial X \partial \tau}$.

It should be emphasized that Equation (48) when combined with (50) gives convenient empirical results for the average concentrations. These equations cannot be used with confidence in conjunction with Equation (40) to determine point concentration.

A graphical summary of the regions of application of the various solutions to Equation (1) is shown in Figure 8. Equations (48) and (50) apply over the entire range where the Taylor-Aris solution holds, as well as over the considerably extended area shown, including the pure diffusion region.

Plots of the dimensionless mixing lengths as a function of τ were also drawn for low Peclet numbers in Figure 7 and they show some interesting results. It is seen that as the Peclet number decreases, there is a gradual change from a curve at N_{Pe} 23,000 to a straight line at $N_{Pe} =$ 1.0. For high Peclet numbers the equations for the left and right branches of the curve (regions 1 and 2, refer-

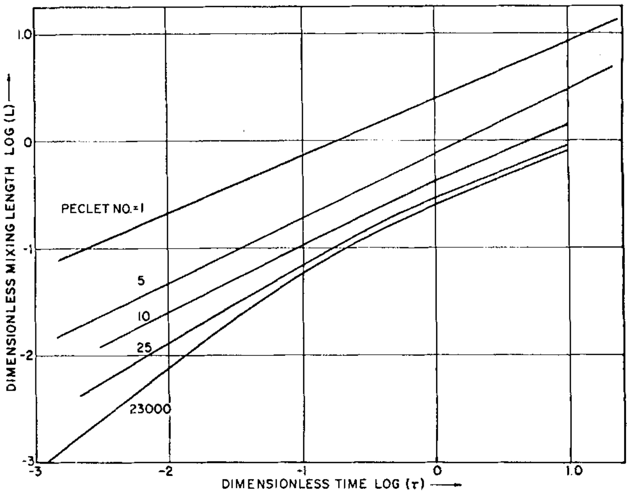

Fig. 7. Plot of mixing length vs. time.

ence 3) are given by $L = 0.8\tau$ and $L = 0.26\tau^{0.50}$, respectively. As regards low Peclet numbers ($N_{Pe} < 100$), it can be seen clearly in Figure 7 that all the curves are nearly parallel, especially in region 2. Therefore, it seems possible to develop a general equation of the form

$$L = \text{constant } (N_{Pe})^a \, (\tau)^b$$

where a and b are constants to be evaluated by cross-plotting procedures. Thus, the following expressions are obtained for low Peclet numbers.

$$\begin{aligned} L &= 2.5\, N_{Pe}^{-0.75}\, \tau^{0.55} \quad \text{for} \quad \tau > 0.05 \\ L &= 2.5\, N_{Pe}^{-0.75}\, \tau^{0.60} \quad \text{for} \quad \tau < 0.05 \end{aligned} \tag{52}$$

These two expressions were tested for a number of points. The average absolute deviation for twenty points was found to be 8% and the maximum deviation occurred for Peclet number = 25 and it was found to be 22%.

It should be pointed out that the C_{avg} vs. τ curves from which the values of L were determined do not resemble generally error function curves nor do they all resemble each other. Thus, there is no equivalent axial dispersion coefficient that can be calculated from these mixing lengths. The idea of the equivalent axial dispersion coefficient is very useful but only when the average concentration is essentially an error function, since it then allows calculation of the complete average concentration distribution from a minimum of data. Our use of the mixing length idea is simply to demonstrate the effects of the parameters τ and N_{Pe}; it is no more useful than the axial dispersion coefficient when checking experiment, designing, etc. For this reason, the numerical results are presented in as much detail as possible for the low Peclet number region.

Applicability of Various Equations

Figure 8, which summarizes the regions of application of the various solutions, can be used to compare the applicability and limitations of the various equations. Taylor (*12*) showed that the conditions under which his approximate solution was valid for laminar flow with radial diffusion only could be expressed as $\frac{4L}{a} >> \frac{Ua}{D} >> 6.9$, where L is the length of the tube over which appreciable changes in concentration occur. The inequality

$$\frac{Ua}{D} >> 6.9 \tag{52a}$$

can be written as

$$N_{Pe} >> 13.8 \tag{52b}$$

Our results from Figure 8 indicate that Taylor's solution is applicable only in the region $N_{Pe} > 100$. Bournia et al. (*5*) found that the minimum velocity for their experimental results (with a 2.17 cm. diameter tube, and diffusivity of 0.039 sq.cm./sec.) to agree with Taylor's solutions was $U = 2$ cm./sec., corresponding to a Peclet number of 110, which is in good agreement with our results.

A second restriction given by Taylor is

$$\frac{4L}{a} >> \frac{Ua}{D} \text{ or } N_{Pe} << \frac{8L}{a} \tag{53}$$

Bournia et al. evaluated $4L/a = 740$ but they contended that Equation (53) is not too important because Taylor's approximation applies best at higher velocities.

The second criterion of Taylor [Equation (53)] does not in fact put an upper limit on N_{Pe} as it seems to. Substituting Taylor's expression for the mixing length

$$L = 3.62\sqrt{kt} \tag{54}$$

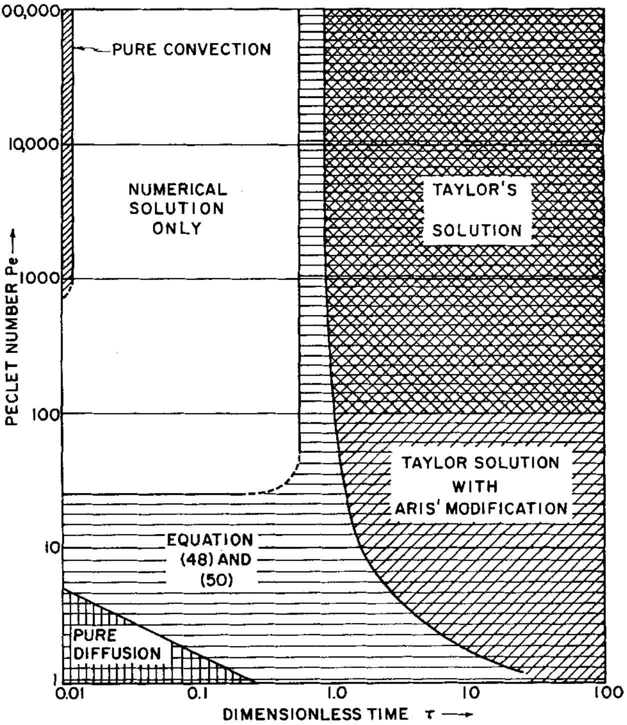

Fig. 8. Graphical summary of the regions of application of solutions.

into Equation (53), one finds the net results to be a lower limit on τ, that is

$$\tau >> 0.25$$

Our numerical results corroborate this and indicate that the lower limit is $\tau = 0.8$ as shown on Figure 8.

As noted before, Taylor's solution is not applicable for Peclet numbers less than 100. In this region Aris (*1*) showed that the effective diffusivity is $K = k + D$. One would hope then that by applying this in the expression for L in Equation (54), one can find the lower limit of τ for all Peclet numbers. The result is

$$\tau >> \frac{0.25\, N_{Pe}^2}{N_{Pe}^2 + 192} \tag{55}$$

and this predicts that as the Peclet number decreases, the lower limit on τ also decreases. From Figure 8, it can be clearly seen that the Taylor-Aris solution holds good for all $N_{Pe} < 100$ but the lower limit on τ actually increases as the Peclet number decreases, as given in Table 1. Hence, Equation (55) predicts the trend in the wrong direction.

The contention of Bournia et al. is that Aris' modification may not account properly for the molecular diffusion at large τ and low N_{Pe}, since their experimental results indicate the K values to be far greater than those obtained by Taylor or Bailey and Gogarty. For the system studied here, our results show that the Taylor-Aris modification does, in fact, describe the solution very well, provided τ is large enough. The lower limits of these τ values are shown on Figure 8 and in Table 1.

In a subsequent paper in this series on laminar dispersion, experimental evidence will be presented which indicates that very small density differences can create significant natural convection effects in very slow flows. Bournia used two gases of the same molecular weight (butyne and butadiene) to eliminate natural convection, but it can be shown that there is possibly enough density difference in this system to account for greatly increased axial dispersion in a vertical tube. For these two gases of the same molecular weight, the maximum value of the

Grashof number in Bournia's 2.17-cm. tube may be shown to be

$$N_{Gr} = 7 \times 10^6 \Delta Z$$

where ΔZ is the difference in the compressibility factors of the two gases. For ΔZ on the order of 10^{-3} to 10^{-4} the Grashof number increases from 700 to 7,000. In horizontal tubes it has been shown experimentally in this laboratory that natural convection affects dispersion strongly in liquid systems at $N_{Gr} = 120$ with slow flows. It thus appears that natural convection can account for the anomalous observations of Bournia.

Finally, the range of applicability of Equations (48) and (50) can be seen in Figure 8. They apply over the entire range where the Taylor-Aris solution holds and also over the considerably extended area shown, including the pure diffusion region. But they do not cover the region unshaded in Figure 8, where numerical solutions must be resorted to, at least for the present. Figures 1*a*, 2, and 6*a* give a few sample numerical results for this region. A complete tabulation of results for this region is available elsewhere.*

CONCLUSIONS

A complete numerical solution to the equation describing laminar flow in tubes with both axial and radial molecular diffusion has been obtained and results for point, average, and bulk concentration distributions are presented for a very wide range of parameters. Numerical solutions were determined for τ from 0.01 to 30 and N_{Pe} from 1 to 23,000. The range of applicability of these results is extended to infinity for both τ and N_{Pe} by the Taylor-Aris theory.

Axial molecular diffusion is significant at lower values of the Peclet number but the magnitude of N_{Pe} at which this occurs depends on the value of τ. In general, axial diffusion is significant at larger values of N_{Pe} as τ decreases and no single value of N_{Pe} can be offered as a criterion for neglecting this effect.

On the basis of our results and in view of Aris' analysis, there is no justification for Bailey and Gogarty's empirical modification which yields an exponent of 0.541 rather than 0.50 for τ in Equations (35) and (36).

Our numerical results for both small and large values of N_{Pe} corroborate the Taylor-Aris asymptotic theory for large values of τ. For the system studied here, no justification was found for the conjecture of Bournia et al. that Aris' low N_{Pe} modification does not account properly for axial diffusion. It was found that the Aris modification is valid for all N_{Pe} provided τ is sufficiently large. The lower limits on τ are given in Table 1 and Figure 8, and it is significant that the magnitude of τ is the only necessary criterion.

Equations (48) and (50) were developed and they express with good accuracy the average concentration over wider ranges of N_{Pe} and τ than any previously reported expressions.

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NOTATION

a = radius of the tube

A = maximum value of $x_{conv}/x_{diff} = N_{Pe}\sqrt{\tau}$

C^+ = point concentration

C_o^+ = initial concentration of the solute

C = dimensionless point concentration C^+/C_o^+

C_M = dimensionless concentration at infinite distance

C_{avg} = dimensionless average concentration

C_{bulk} = dimensionless bulk concentration

D = molecular diffusion coefficient

k = effective axial diffusivity of Taylor, $\dfrac{a^2u_o^2}{192D}$

K = effective diffusivity $k + D$

K_1 = $(\tau/48) + (4\tau/N^2_{Pe})$

L = dimensionless mixing zone length, $\dfrac{D}{a^2u_o}L'$

L' = mixing length = Δx between $C^+/C_o^+ = 0.1$ to 0.9

M = total number of intervals in η direction

N = total number of intervals in y direction

N_{Pe} = Peclet number $\dfrac{au_o}{D}$

P = parameter $\dfrac{1}{N^2_{Pe}} + Q$

Q = numerical variable ranging from 0 to 1/192

r = radial distance

t = time through which the solute disperses

U = average velocity $u_o/2$

u_o = maximum velocity at center of the tube

x = axial distance along the tube

X = dimensionless axial coordinate, $\dfrac{D}{a^2u_o}x$

x_1 = axial distance relative to axes which move with mean flow, $x - 1/2\ u_o t$

x_{conv} = pure convective length, $u_o t$

x_{diff} = pure diffusive length, $\sqrt{Dt}$

y = dimensionless radial coordinate r/a

Subscripts

i = interval in the η direction

j = interval in the y direction

n = interval in the τ direction

Greek Letters

Δ = the incremental value of any variable

η = dimensionless axial coordinate,

$$\frac{x}{\sqrt{\tau}} = \frac{x}{au_o}\sqrt{\frac{D}{t}}$$

τ = dimensionless time, (Dt/a^2)

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* See footnote on page 1065.