

X = Martinelli momentum transfer parameter $[(dP/dL)_L/(dP/dL)_G]^{1/2}$, dimensionless
 x = mole fraction solute in liquid, dimensionless
 y = mole fraction solute in gas, dimensionless
 y^* = composition of vapor in equilibrium with annular liquid; defined by Equation (6), dimensionless
 μ = fluid viscosity, lb. mass/(ft.) (hr.)
 ρ = fluid density, lb. mass/cu.ft.

Subscripts

a = annular liquid film
 e = entrained liquid
 G = gas phase
 L = liquid phase

LITERATURE CITED

- Alves, G. E., *Chem. Eng. Progr.*, **50**, 449 (1954).
- Blasius, H., *Mitt. Forschungsarb.*, **131**, 1 (1913).
- Budd, J. T., B.Ch.E. thesis, Univ. Del., Newark, Delaware (1950).
- Bertuzzi, A. F., M. R. Tek, and F. H. Poettmann, *Trans. Am. Inst. Mining Engrs.*, **207**, 17 (1956).
- Calvert, S., and B. Williams, *A.I.Ch.E. Journal*, **1**, 78 (1955).
- Charvonia, D. A., Project Squid, *Technical Rept. PUR-39-T-R* (1959).
- Chenoweth, J. M., and M. W. Martin, *Petrol. Refiner*, **34**, 151 (1955).
- Chilton, T. H., and A. P. Colburn, *Ind. Eng. Chem.*, **26**, 1183 (1934).
- Colburn, A. P., *ibid.*, **22**, 967 (1930).
- Emmert, R. E., M.Ch.E. thesis, Univ. Del., Newark, Delaware (1952).
- Fritzlen, A. F., M.Ch.E. thesis, Univ. Del., Newark, Delaware (1951).
- Hoogendoorn, C. J., *De Ingenieur*, **46**, p. 81 (1959).
- Isbin, H. S., R. H. Moen, and D. R. Mosher, *A.E.C.U.* 2994 (1954).
- Lockhart, R. W., and R. C. Martinelli, *Chem. Eng. Progr.*, **45**, 39 (1949).
- McManus, H. N., Ph.D. thesis, Univ. Minn., Minneapolis, Minnesota (1956).
- Sherwood, T. K., and R. L. Pigford, "Absorption and Extraction," McGraw Hill, New York (1952).
- White, P. D., and R. L. Huntington, *Petrol. Eng.*, **27**, D 40 (1955).
- Wicks, M., and A. E. Dukler, *A.I.Ch.E. Journal*, **6**, 463 (1960).

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Longitudinal Dispersion of Thermal Energy Through Porous Media with a Flowing Fluid

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The rate of heat transfer in porous media with a flowing fluid present is determined by a combination of mechanisms. Broadly these may be grouped as bulk movement of the fluid, conduction in the solid and fluid phases, convective transfer of heat between the phases, convective eddy mixing or dispersion of the fluid phase in the porous-media interstices, and radiation.

A well-known example of the effect of these mechanisms in porous-media heat transfer is illustrated in Figure 1. A fluid at temperature T_0 is flowing in one-dimensional, steady, piston flow through a homogeneous, stationary porous prism, also at temperature T_0 . At the point $x = 0$ the temperature of the input fluid is suddenly changed to a new value T_i and held constant. A thermocouple, placed at $x = L$, will yield an S shaped response curve as the heat front arrives, not a step function as was introduced into the prism. Thermal energy will have dispersed in the direction of fluid flow and away from the step-function position, the amount of dispersion being determined by the heat transfer mechanisms which are important at the particular conditions of the experiment.

In the late 1920's Anzelius (2), Schumann (27), and others (16, 23) presented papers dealing with the mathematical description of heat flow by bulk fluid movement

with convective transfer between solid and fluid phases. These works showed that as a consequence of the finite time required for heat transfer between the phases there was a dispersion of the energy giving rise to a characteristic S shaped temperature-response curve with a step-function input.

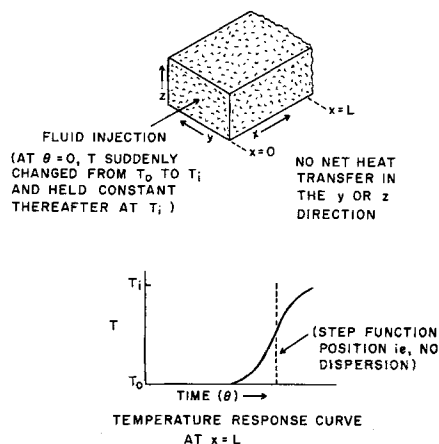


Fig. 1. Longitudinal heat transfer in porous media.

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It is also known that the presence of other heat transfer mechanisms results in temperature profiles of the same general form. Molecular conduction in one or both phases, superimposed on the bulk fluid flow, is one dispersion means (17). Furthermore dispersion of heat by a convective mixing process occurs in packed beds owing to the irregularities of fluid flow since fluid elements undergo a series of events such as acceleration, deceleration, or temporary trapping in eddies or stagnation points. Velocity profiles which develop in the interstices also tend to cause a spread of the thermal energy. These effects have been investigated by several workers in the area of mass transfer (4, 5, 7, 10, 20), and in nearly all cases the diffusivity equation has been used to fit experimental data with molecular diffusivity being replaced by an eddy-dispersion coefficient.

Examination of the general problem in which the different modes of heat transfer (for example conduction and convective transfer between phases) act simultaneously has also shown that the S shaped response curve results (1, 15, 26, 31). Unfortunately the relative contributions of each to the overall rate are not easily determined from experimental data, since measured temperature profiles have the same form for the individual mechanisms and for a combination of these. Only a very limited amount of data have been taken and analyzed for this latter case. The importance of interactions of the mechanisms has seldom been examined.

The present work was undertaken for the specific purpose of theoretically and experimentally examining longitudinal unsteady state heat transfer at relatively low fluid velocities and low temperatures where radiation is unimportant. One-dimensional, piston, liquid flow was primarily investigated.

THEORETICAL INVESTIGATION

When one considers a physical system as shown in Figure 1, an energy balance over a porous-medium increment yields the differential equations: for the fluid phase

$$\rho_w C_w \phi \frac{\partial T_w}{\partial \theta} = -v \rho_w C_w \phi \frac{\partial T_w}{\partial x} + k_w \phi \frac{\partial^2 T_w}{\partial x^2} - ha (T_w - T_s) \quad (1)$$

for the solid phase,

$$\rho_s C_s (1 - \phi) \frac{\partial T_s}{\partial \theta} = k_s (1 - \phi) \frac{\partial^2 T_s}{\partial x^2} + ha (T_w - T_s) \quad (2)$$

Here k_s is a pseudo thermal conductivity characterizing the rate of apparent solid-phase conduction in the longitudinal direction. The fluid-phase coefficient k_w includes both a conduction contribution and the effect of eddy dispersion

$$k_w = k_{wc} + k_{wm} \quad (3)$$

Of these coefficients k_{wm} is a function of fluid flow rate, while k_{wc} and k_s are assumed to be static contributions, independent of fluid velocity.

The rate of heat transfer between the solid and fluid phases at any point is assumed proportional to their average temperature difference, ha being the constant of proportionality. An implicit assumption in the differential equations is that temperature gradients within the solid normal to the fluid-flow direction are nonexistent; that is the resistance to heat transfer between fluid and solid lies entirely within a fluid film around the solid.

Applicable boundary conditions for the model are

$$\begin{aligned} T_w &= T_s = T_0, \text{ all } x, \theta = 0 \\ T_w &= T_s = T_i, x = 0, \text{ all } \theta > 0 \\ T_w &= T_s = T_0, x \rightarrow \infty, \text{ all } \theta \end{aligned} \quad (4)$$

An analytical solution to the differential equations could not be obtained. However numerical calculations for several specific values of the system parameters were made with an IBM-650 digital computer, and results were previously reported (14, 15). Numerical calculations were time consuming and rather impractical for use in the evaluation of experimental data. Therefore an approximate solution was derived which in many instances allows the heat transfer to be well represented with the diffusivity equation and an overall effective thermal conductivity.

The derivation of the approximate solution to the general differential equations follows the work of Klinkenberg and Sjenitzer (19), and Van Deemter et al. (31). It is described in detail elsewhere (14). The approximation is based on the fact that for a pulse thermal-energy input into a packed bed the heat or mass transfer mechanisms of molecular conduction, eddy dispersion, and convective transfer between phases all individually give rise to Gaussian distributions in the bed thermal-energy holding-time variable. This is true under prescribed conditions of bed parameter sizes. When these transport mechanisms act simultaneously in a system, it is postulated that the distribution of holding times is still normal, and the individual variances for the distributions are simply additive. The development is thus based on the assumption that the separate mechanisms act in a statistically independent manner, and application is made of the general principle of probability theory that the variance of the sum of two or more statistically independent random variables is the sum of the individual variances. This assumption results in the following approximate solution for the injection of an energy pulse $[\rho_w C_w \phi v (T_i - T_0) \theta_0]$ over the small time increment θ_0 , into a packed bed initially at the temperature T_0 :

$$\frac{t_w}{\theta_0} = \frac{1}{\sqrt{2\pi\sigma^2}} \exp \left[-\frac{\left(\frac{x}{V_F} - \theta\right)^2}{2\sigma^2} \right] \quad (5)$$

with

$$\sigma^2 = \sigma_1^2 + \sigma_2^2 + \sigma_3^2 + \dots \quad (6)$$

For the specific mechanisms considered here

$$\sigma^2 = \frac{2 k_e^o x}{\rho_w C_w \phi v V_F^2} + \frac{2 k_{wm} \phi x}{\rho_w C_w \phi v V_F^2} + \frac{2 [\rho_s C_s (1 - \phi)]^2 x}{\rho_w C_w \phi v ha} \quad (7)$$

From Equation (7) it is seen that an apparent longitudinal effective conductivity for the heat transfer coefficient contribution to the dispersion may be defined as

$$k_{ha} = \frac{V_F^2 [\rho_s C_s (1 - \phi)]^2}{ha} \quad (8)$$

reducing Equation (7) to

$$\sigma^2 = \frac{2xK}{V_F^3} \quad (9)$$

where

$$K = \frac{k_e^o + k_{wm} \phi + k_{ha}}{\rho_w C_w \phi + \rho_s C_s (1 - \phi)} \quad (10)$$

Thus an overall effective thermal conductivity k_e is defined as

$$k_e = k_e^o + k_{wm} \phi + k_{ha} \quad (11)$$

A corresponding form of the approximate solution for a step-function temperature input is, after one rearranges the error-function argument and substitutes θ for x/V_F in the denominator of the argument

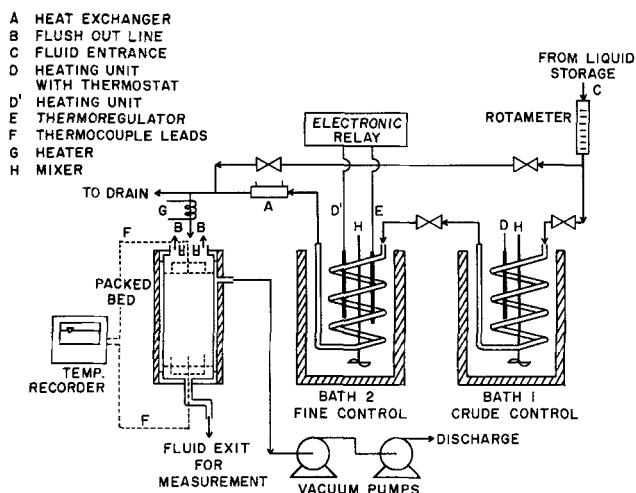


Fig. 2. Flow system.

$$t_w = \frac{1}{2} \left[1 - \operatorname{erf} \left(\frac{x - V_F \theta}{2\sqrt{K\theta}} \right) \right] \quad (12)$$

The substitution of θ for x/V_F is valid as long as the dispersion away from the mean position is relatively small. The applicability of Equation (12) was checked by a comparison with the numerical solution previously mentioned. Agreement between the two solutions was satisfactory as long as the condition

$$\frac{2k_e}{\rho_w C_w \phi v x} \ll 1 \quad (13)$$

was satisfied.

EXPERIMENTAL INVESTIGATION

The experimental model was designed to simulate the basic requirements of the real physical system under consideration. The main requirements were: piston flow of a liquid in one direction (longitudinal) through a homogeneous packed bed, the establishment of a known initial constant temperature throughout the bed, the introduction of a step function in temperature into one end of the packed section, measurement of the response temperature profile at a known position down the bed, and negligible heat losses in the direction perpendicular (radial) to the fluid flow.

A schematic diagram of the flow system is shown in Figure 2. The packed heat-transfer tube was approximately 14 in. in length and 3.7 in. in diameter. An open-volume section immediately above the packed bed and a flow sparger served to distribute the flow evenly across the inlet. A step-function temperature input was approximated by first bringing the bed to a desired temperature T_0 with the test liquid as heating media. Then the entrance-face temperature was quickly changed by flushing out the open-volume section above the bed with liquid at a different input temperature T_i . Experimental checks and calculations indicated that this procedure gave a satisfactory step-function input. The response temperature profile of the porous media to the step-function input was measured by inserting thermocouples at known positions in the packed bed.

Heat losses from the experimental section was minimized by insulating the heat transfer tube with a vacuum on the order of 0.5 mm. Hg absolute pressure. A radiation shield further reduced losses. The heat transfer tube was made of thin-walled (0.010 in.) stainless-steel sheet resulting in low wall heat capacity and negligible conduction down the tube in the direction of fluid flow.

To check for entrance effects, that is for changing dispersion conditions with length of travel in the porous media, thermocouples were located at positions of 6.8 and 11.0 in. from the bed entrance. Statistical comparison of the data at these points indicated that the dispersion characteristics were not changing significantly with length of travel. This is in agreement with previously reported results (6, 10, 28).

Gross Velocity Profiles

The possibility of the presence of significant deviations from piston flow in the tube was examined by placing several thermocouples at the same height but at different radial positions. Deviations from piston or plug flow would result in radial temperature gradients, as radial heat flow would not be of sufficient magnitude to erase any large gradients. Since temperature response curves were measured at points in the bed and an average or mixing-cup value was not used, any small deviations from piston flow should not significantly affect the results.

Tube-Wall Effects. It is known that the tube wall can induce nonplug fluid flow in a packed bed. Flow deviates more from piston flow in a given tube as the particle size is increased. Reported experimental studies (22, 28, 29) have shown that as long as the ratio d_p/d_t (particle diameter/tube diameter) is less than about 0.04 the assumption of plug flow is good. In this work the ratio did not exceed 0.032. Furthermore the presence of this effect would have resulted in radial symmetrical temperature gradients, and no such gradients were observed.

Channeling. A distortion of the flow pattern termed *channeling* sometimes occurs in porous media. Petroleum engineers are familiar with this phenomenon in systems where the viscosity ratio is unfavorable (3); that is when the fluid being displaced has a higher viscosity than the displacing fluid, channeling nearly always results. In the present case channeling due to an unfavorable viscosity ratio did occur when hot liquid displaced cold liquid from the packed bed. This channeling was indicated by the presence of large unsymmetrical radial temperature gradients. When cold liquid displaced hot (cooling run experiments), the flow front was evidently flat as evidenced by a flat radial temperature profile. For this reason cooling run experiments were of primary interest. Data taken at conditions where channeling was present owing to an unfavorable viscosity ratio are reported elsewhere (14).

Experimental Materials and Condition

Four different liquids were used in the experimental program. These were distilled water, 30% by wt. glycerol (aqueous), 60% by wt. glycerol (aqueous), and ethyl alcohol. Solid glass spheres made up the packed bed with four sizes being used, 0.0038, 0.0181, 0.0425, and 0.118 in. in diameter. Average interstitial velocities were between 2 and 25 ft./hr., and the temperature range did not exceed 70° to 180°F.

INTERPRETATION AND PRESENTATION OF EXPERIMENTAL RESULTS

Experimental data, consisting of the measured temperature response curves, were used to calculate values of the overall effective thermal conductivity k_e defined in the approximate solution previously discussed, Equations (10) through (12).

To evaluate k_e use was made of the fact that for the function

$$y = \operatorname{erf}(bx) \quad (14)$$

a plot of y vs. x on arithmetic probability paper (y plotted on probability scale) yields a straight line. Therefore from Equation (12) a graph of t_w vs. $(x/\sqrt{\theta} - V_F\sqrt{\theta})$ should be linear. A typical curve is shown in Figure 3 from which k_e may be determined by first reading F values at any two selected points, for example at $t_w = 0.1$ and $t_w = 0.9$. Then from tables of the error function k_e is calculated with the difference in the error function arguments at these two points, since all other parameters are known. This method determines k_e from the spread in time or dispersion of the measured temperature response curves.

The experimental curve of Figure 3 does not cross the zero F value exactly at a temperature fraction of 0.5 as required by Equation (12). This is so for two reasons: Equation (12) is an approximation, the more rigorous solution requiring a displacement of the zero F value in the direction shown, and there is a small error in the values of the parameters (such as v , ρ_s , C_s , etc.) used to calculate F .

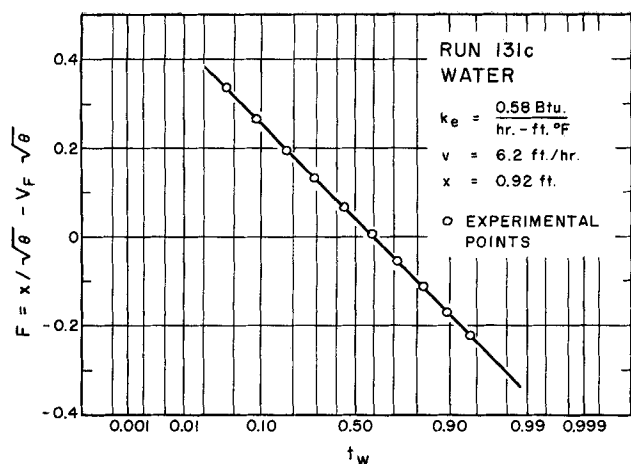


Fig. 3. Calculation of k_e ; t_w vs. F on probability paper.

Effective thermal conductivities were calculated for all cooling runs in which no flow channeling occurred. A plot of k_e vs. the product of velocity and particle diameter vd_p for each liquid system was found to give a smooth continuous curve over all particle sizes investigated. In Figure 4 these results are shown for the water system. Data scatter is on the order of ± 5 to $\pm 8\%$. Plotting k_e as a function of Reynolds number was not satisfactory, as the introduction of viscosity caused the data to scatter.

SUMMATION OF CONDUCTIVITIES

The theoretical analysis indicated that the coefficients expressing the individual dispersion mechanisms were additive in accordance with Equation (11). The approximation was stated to be applicable as long as the condition $(2k_e/\rho_w C_w \phi v x) \ll 1$ was met. Maximum experimental values of this group were generally in the range of 0.01 to 0.025, sufficiently small for application of the approximation. The experimental data described above were therefore used to test the model.

The static component k_e^o of the overall effective conductivity was calculated by extrapolation of k_e data to zero velocity. The velocity dependent component, defined as

$$k_e(v) = k_e - k_e^o \quad (15)$$

was assumed to be the sum of the film resistance k_{ha} and the eddy dispersion contribution k_{wm} . Existing literature data on solid-fluid heat and mass transfer were used to determine the magnitude of the film resistance. An eddy-dispersion contribution was then calculated as the remainder of $k_e(v)$ after subtraction of k_{ha} , and a correlating curve was developed for k_{wm} . Eddy-dispersion values thus obtained are shown to be consistent with longitudinal mass transfer data in the literature.

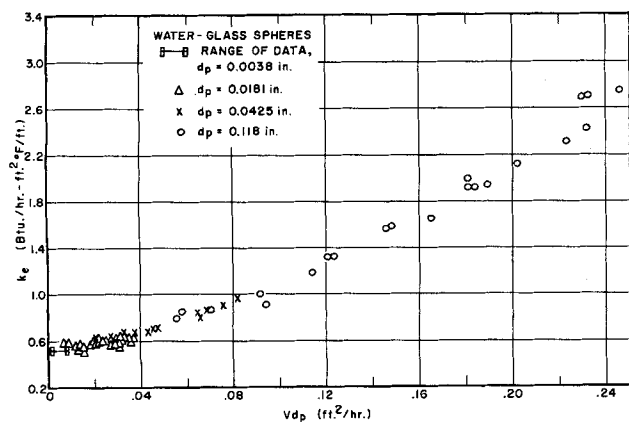


Fig. 4. Effective thermal conductivity vs. vd_p ; water system.

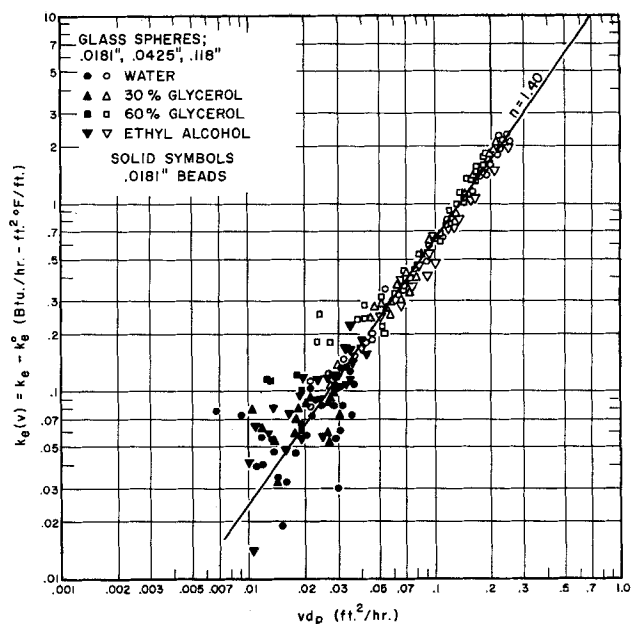


Fig. 5. Velocity component of the effective thermal conductivity; all liquid systems.

Static Thermal Conductivity

The static component of the effective thermal conductivity was not measured directly in the experimental program. These data were obtained by extrapolation of k_e values to zero velocity. Values of k_e^o thus determined were in good agreement with the predictive equation of Euchen (11) except for the ethyl alcohol system where the predicted value was low. Calculated and extrapolated values are presented in Table 1.

Preston (24) measured k_e^o in porous-media systems very similar to those of this investigation. Glass-water and glass-20% aqueous glycerol systems were included in the Preston investigation, and the reported k_e^o values are within 4% of the water and 30%-glycerol extrapolated values of this work. Application of Preston's predictive equation to ethyl alcohol yields a k_e^o of 0.41, substantiating the extrapolated number found in this work.

Velocity Component $k_e(v)$

Calculated velocity components of k_e defined by Equation (15) are plotted for all systems on log-log paper as a function of vd_p in Figure 5. The $k_e(v)$ data for the smallest glass beads used, 0.0038 in., are not shown on the graphs. Data scatter increases markedly as vd_p decreases, since k_e^o becomes the major portion of k_e and $k_e(v)$ is obtained as the difference between two numbers of the same order of magnitude.

A linear fit to all the data points in the experimental series with the two largest bead sizes resulted in the equation

$$k_e(v) = 16 (vd_p)^{1.4} \quad (16)$$

At the larger values of vd_p the data fit Equation (16) within $\pm 14\%$. As seen from the discussion which follows

TABLE 1. STATIC THERMAL CONDUCTIVITIES

Liquid system	Extrapolated k_e^o	Euchen equation k_e^o	ϕ
Water	0.51	0.49	0.355
30% glycerol (aqueous)	0.50	0.45	0.355
60% glycerol (aqueous)	0.45	0.41	0.355
Ethyl alcohol	0.40	0.27	0.355

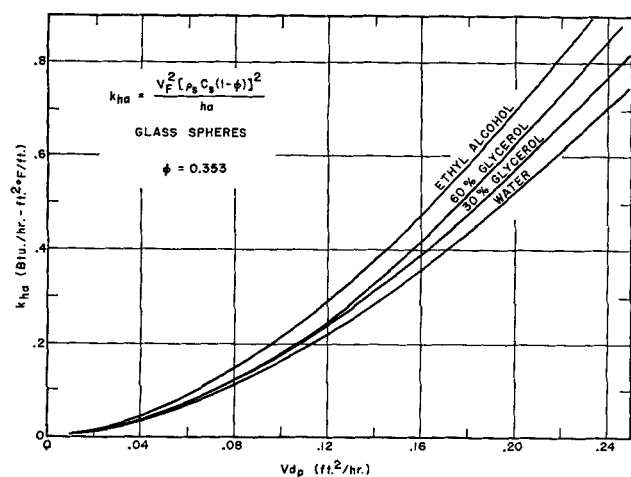


Fig. 6. k_{ha} vs. $v_d p$; heat transfer coefficient data from Dryden, Strang, Withrow.

the excellent fit of the data to this equation is fortuitous. A significant change in system properties such as fluid physical properties, bead size, or bead physical properties would result in deviations from this curve.

Solid-Fluid Heat Transfer. The solid-fluid film resistance component of $k_e(v)$ was defined by Equation (8). To calculate ha the empirical correlating curve (j_m vs. N_{Re}) of Dryden, Strang, and Withrow (9) was used. This curve was selected primarily because Dryden et al. obtained transfer-coefficient data in liquid systems at low flow rates, and furthermore the data are in good agreement with other available results. The particle surface area per unit volume of bed was calculated from

$$a = \frac{6(1 - \phi)}{d_p} \quad (17)$$

In Figure 6 a typical plot of k_{ha} vs. $v_d p$ as determined from the curve of Dryden et al. is shown.

Other applicable correlations could be applied to determine the heat transfer coefficient (32, 33) and correspondingly k_{ha} . In reference 14 the data of Yoshida et al. (33) were used in addition to the Dryden et al. curve, resulting in k_{ha} values on the order of 15 to 30% higher than those obtained from the Dryden et al. correlation.

Solid-phase, intraparticle resistance to heat transfer results in longitudinal dispersion in the same manner as the fluid film resistance. With results derived from the work of Deisler (8) used, this effect was estimated to be something less than 10% of the total measured k_e for the investigated systems (14). While the magnitude is noteworthy, the contribution of the intraparticle resistance is considerably smaller than that of the other mechanisms. At its maximum contribution it is just at the limits of experimental error. This effect was therefore assumed negligible.

Eddy Dispersion. The eddy-dispersion contribution to the longitudinal dispersion was calculated as the difference between $k_e(v)$ and k_{ha} . While no thermal-energy eddy-dispersion data at the experimental conditions of this investigation are available in the literature for comparison, several studies have been made for mass transfer. In Figure 7, data from this study for the water and alcohol systems, as well as the literature mass-transfer data, are shown as a plot of N_{Pe} vs. N_{Re} , where

$$N_{Pe} = \frac{v d_p}{E + D} \quad (18)$$

and for heat transfer

$$E_h + D_h = \frac{(k_{wm}\phi + k_{wc}\phi)}{\rho_w C_w \phi} \quad (19)$$

This plot is only for comparison purposes. The heat transfer results are in good agreement with the gas-phase mass transfer work of McHenry and Wilhelm (21) and are somewhat below the Peclet number values of Deisler (8). Heat transfer Peclet numbers are considerably above those for eddy dispersion of mass in liquid systems. For the systems shown the molecular contributions are as follows: D_m is negligible in the liquid-phase mass transfer data, D_m is approximately 30% of $(E_m + D_m)$ in the gas-phase mass transfer data at a Reynolds number of 27, and D_h is about 8% of $(E_h + D_h)$ in the heat transfer results at a Reynolds number of 11. The relative importance of D increases with increasing N_{Re} .

In accordance with the model of Keulemans (18) for eddy dispersion

$$E = \eta v d_p \quad (20)$$

where η is a constant characteristic of the porous medium. At the same Reynolds number therefore two geometrically similar packed-bed systems should have the same η value,

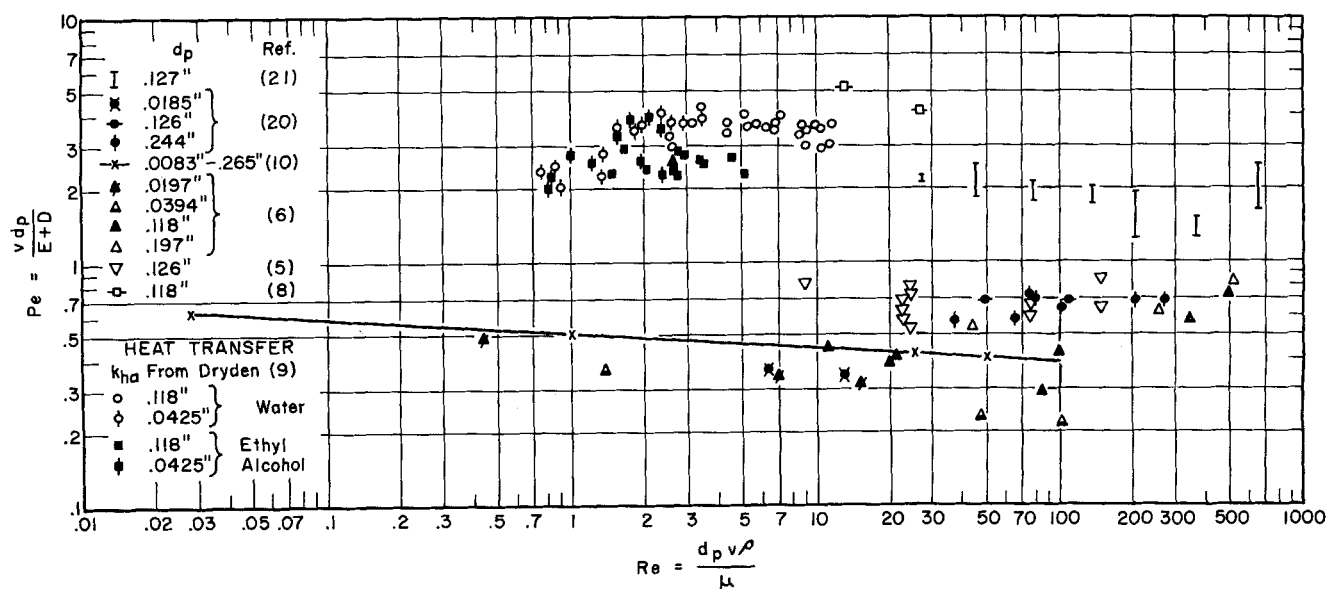


Fig. 7. Peclet number vs. Reynolds number; heat and mass transfer data.

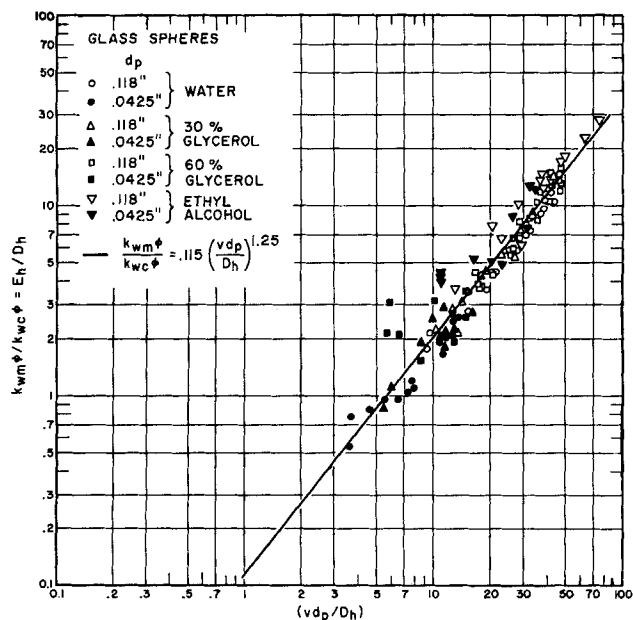


Fig. 8. Correlation of eddy-dispersion data; E/D vs. (vd_p/D) ; k_{ha} from Dryden, Strang, Withrow data.

resulting in the Peclet numbers being equal for the two systems (provided molecular diffusivities are equal). However mass transfer results with liquids and gases are quite different, necessitating an explanation.

A proposed reason has been discussed by several authors (3, 12, 13) and is based on the results obtained by Taylor (30) for dispersion in flow through a capillary tube. Because of velocity profiles which develop in the pores and due to fluid trapping, etc., some of the fluid in the pores will be bypassed by the displacing fluid, at least temporarily. This bypassed fluid will approach the main stream concentration by a molecular conduction process. The result of this bypassing is a greater longitudinal dispersion of mass, the dispersion becoming greater as the molecular diffusivity is decreased. Conversely if the fluid has a very high molecular diffusivity, concentration gradients normal to the flow direction which result because of bypassing will be quickly diminished and the resulting longitudinal eddy dispersion will be reduced. This effect is characterized by (12)

$$E \propto \frac{v^2}{D} \quad (21)$$

Thus on this basis the difference between the gas- and liquid-phase mass transfer data is at least qualitatively explained.

For the case of heat transfer the molecular thermal diffusivity lies intermediate to the values of liquid and gas mass diffusion. In addition molecular conduction through the solid particles, as well as conduction from the bulk fluid, will act to bring the bypassed fluid up to the main-stream temperature. Therefore the effect of molecular conduction through the solid should be to decrease the longitudinal eddy dispersion. Qualitatively then, with liquids flowing, the eddy-dispersion coefficient for heat transfer would be expected to be smaller than for the corresponding mass transfer case. This was the result obtained experimentally. The two mechanisms, Equations (20) and (21), are not additive, but a correlating equation of the following form is suggested (3):

$$\frac{E}{D} = n \left(\frac{vd_p}{D} \right)^m \quad (22)$$

where n and m are constants obtained from experimental

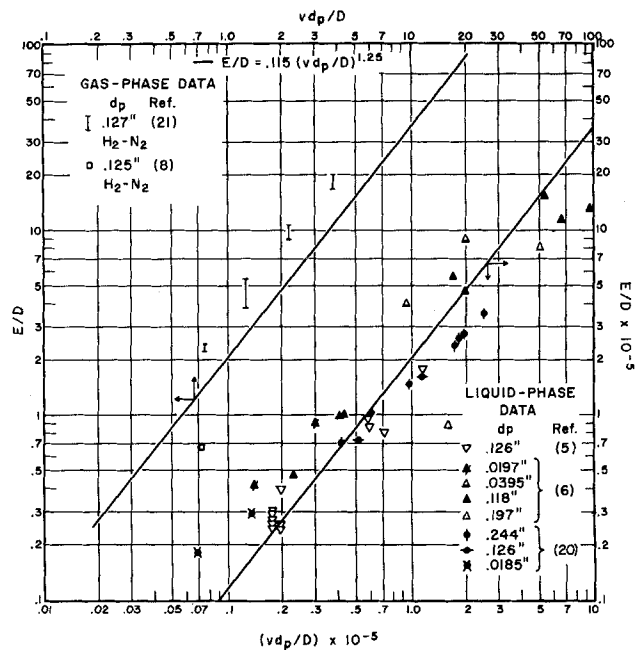


Fig. 9. Comparison of Equation 23 with mass transfer data.

data and where m is greater than 1. The $k_{wm}\phi$ data are plotted in Figure 8 with E/D as a function of vd_p/D . A least-squares fit to all the data with a vd_p value greater than 0.03 yielded $n = 0.115$ and $m = 1.25$:

$$\frac{E}{D} = 0.115 \left(\frac{vd_p}{D} \right)^{1.25} \quad (23)$$

This curve is also shown in Figure 8.

Equation (23) was tested against the mass transfer data of several investigators. The comparison is presented in Figure 9. The gas-phase dispersion data of McHenry and Wilhelm (21) and Deisler (8) are shown, as are the results of representative liquid-phase dispersion investigations (5, 6, 20). Over this wide range of fluid systems Equation (23) does appear to correlate satisfactorily the effect of the fluid-phase molecular diffusivity. However as previously discussed conduction through the solid particles should act to decrease the measured eddy-dispersion coefficient in the case of heat transfer. This effect has not been included in Equation (23). Further investigation with solid packing of different characteristics is required to establish the importance of this solid-conduction mechanism.

CONCLUSIONS

The following conclusions may be drawn from the results of this investigation.

1. The solution to the general differential equations, which include several mechanisms for transient longitudinal dispersion of thermal energy, may be approximated by a simple diffusivity-equation solution with an effective thermal conductivity which is equal to the sum of the contributing conductivities. These contributing conductivities are each a measure of a separate mechanism. This is true within prescribed conditions of parameter sizes.

2. Experimental, longitudinal, thermal-energy dispersion data fit the diffusivity-equation solution as long as piston flow occurred. Values of the effective thermal conductivity k_e calculated from the data substantiate the additivity of the individual contributing conductivities: k_e^o , $k_{wm}\phi$, and k_{ha} .

3. Values of k_e obtained from data for a given liquid increase as a smooth function of the product of interstitial

velocity and particle size, that is vd_p . For the systems studied, at vd_p values less than about 0.01, k_e may be assumed a constant equal to the static conductivity k_e^o with only small error.

4. The correlation developed for eddy dispersion adequately describes the effect of the molecular diffusivity on the eddy-dispersion coefficient. The effect of solid-phase conduction on eddy dispersion should be investigated further.

ACKNOWLEDGMENT

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NOTATION

- a = particle area per unit bed volume, sq.ft./cu.ft.
 b = constant
 C = heat capacity, B.t.u./ (lb.) (°F.)
 D = molecular diffusivity, $k_{wc}/\rho_w C_w$ for fluid-phase heat transfer, sq.ft./hr.
 d_p = particle diameter, in. or ft.
 d_t = inside diameter of tube, ft.
 E = eddy-dispersion diffusivity, $k_{wm}\phi/\rho_w C_w\phi$ for heat transfer, sq.ft./hr.
 erf = error function
 F = $X/\sqrt{\theta} - V_F \sqrt{\theta}$
 h = heat transfer coefficient, B.t.u./ (hr.) (sq. ft.) / (°F.)
 j = empirical j factor
 K = effective thermal diffusivity of porous media, $k_e/[\rho_w C_w\phi + \rho_s C_s(1 - \phi)]$, sq.ft./hr.
 k_e = effective thermal conductivity of porous media, B.t.u./hr. (sq. ft.) / (°F./ft.)
 k_e^o = static thermal conductivity of porous media, that is thermal conductivity of porous media with fluid in place but not moving, B.t.u./ (hr.) (sq. ft.) / (°F./ft.)
 $k_e(v)$ = velocity dependent component of the effective thermal conductivity, B.t.u./ (hr.) (sq. ft.) / (°F./ft.)
 k_{ha} = effective dispersion coefficient characterizing a finite heat transfer rate between the fluid and solid phases of porous media, heat-transfer rate controlled by fluid film around particle, Equation (8), B.t.u./ (hr.) (sq. ft.) / (°F./ft.)
 k_s = pseudo thermal conductivity of the solid phase of porous media, B.t.u./ (hr.) (sq. ft.) / (°F./ft.)
 k_w = pseudo thermal conductivity of the fluid phase, Equation (3), B.t.u./ (hr.) (sq. ft.) / (°F./ft.)
 k_{wm} = eddy-dispersion coefficient, B.t.u./ (hr.) (sq. ft.) / (°F./ft.)
 k_{wc} = molecular thermal conductivity of fluid, B.t.u./ (hr.) (sq. ft.) / (°F./ft.)
 N_{Pe} = Peclet number, $vd_p/E + D$
 N_{Re} = Reynolds number, $d_p v \rho_w / \mu$
 T = temperature, °F.
 t = accomplished temperature fraction, $T - T_o / T_i - T_o$
 v = fluid interstitial velocity, ft./hr.
 V_F = heat-front velocity, $V_F = \frac{\rho_w C_w \phi v}{\rho_w C_w \phi + \rho_s C_s(1 - \phi)}$ ft./hr.
 x = distance, ft.

Greek Letters

- η = empirical constant, Equation (20)
 θ = time, hr. or min.
 θ_o = small increment of time, hr. or min.
 μ = viscosity, lb.m/ft.-hr.
 ρ = density, lb.m/cu.ft.

- ϕ = porosity, that is packed-bed void fraction
 σ = standard deviation, σ^2 defined in Equation (6)

Subscripts

- h = heat transfer coefficient or constant
 i = inlet fluid conditions, at $x = 0$
 m = mass transfer coefficient or constant
 o = initial conditions, at $\theta = 0$
 s = solid phase
 w = fluid phase
 wc = molecular conductivity of fluid
 wm = eddy dispersion

LITERATURE CITED

- Amundson, N. R., *Ind. and Eng. Chem.*, **48**, 26 (1956).
- Anzelius, A., *Zeit. fur angew. Math. und Mech.*, **6** (1926).
- Brigham, W. E., P. W. Reed, and J. N. Dew, *Soc. Petrol. Engrs. Journal*, **1**, 1 (1961).
- Cairns, E. J., Ph.D. thesis, University of California, Berkeley, California (1959).
- , and J. M. Prausnitz, *Chem. Eng. Sci.*, **12**, 20 (1960).
- Carberry, J. J., and R. H. Bretton, *A.I.Ch.E. Journal*, **4**, 367 (1958).
- Danckwerts, P. V., *Chem. Eng. Sci.*, **2**, 1 (1953).
- Deisler, Paul F., Jr., and Richard H. Wilhelm, *Ind. and Eng. Chem.*, **45**, 1219 (1953).
- Dryden, C. E., D. A. Strang, and A. E. Withrow, *Chem. Eng. Progr.*, **49**, 191 (1953).
- Ebach, Earl A., and Robert R. White, *A.I.Ch.E. Journal*, **4**, 161 (1958).
- Euchen, A., *VDI Forschungsheft 353*, Forschung auf dem Gebiete des Ingenieurwesens Ausgabe B (1932).
- Frankel, S. P., "Mixing of Fluid Flowing in a Porous Medium," Conference on Theory of Fluid Flow in Porous Media, University of Oklahoma (March 23-24, 1959).
- Gottschlich, C. F., *A.I.Ch.E. Journal*, **9**, No. 1, p. 88 (January, 1963).
- Green, D. W., Ph.D. thesis, University of Oklahoma, Norman, Oklahoma (1962).
- , and R. H. Perry, *Chem. Eng. Progr. Symp. Ser. No. 32*, **57**, p. 61 (1961).
- Hausen, H. A., *Math. Mech.*, **9**, 173 (1929).
- Jenkins, R., and J. S. Aronofsky, "Analysis of Heat Transfer Processes in Porous Media—New Concepts in Reservoir Heat Engineering," 18th Technical Conference on Petroleum Production at Penn. State Univ. (October 6-8, 1954).
- Keulemans, A. I. M., "Gas Chromatography," Reinhold, New York (1959).
- Klinkenberg, A., and F. Sjenitzer, *Chem. Eng. Sci.*, **5**, 258 (1956).
- Liles, A. W., and C. J. Geankoplis, *A.I.Ch.E. Journal*, **6**, 591 (1960).
- McHenry, K. W., Jr., and R. H. Wilhelm, *ibid.*, **3**, 83 (1957).
- Morales, M., C. W. Spinn, and J. M. Smith, *Ind. and Eng. Chem.*, **43**, 225 (1951).
- Nusselt, W. Z., *Ver. deut. Ing.*, **71**, 85 (1927).
- Preston, F. W., Ph.D. thesis, Penn. State Univ., University Park, Pennsylvania (1957).
- Rosen J. B., and W. E. Winsche, *J. Chem. Phys.*, **18**, 1587 (1950).
- Saunders, O. A., and H. Ford, *Iron and Steel Institute*, **141**, 291 (1940).
- Schumann, T. E. W., *J. Franklin Inst.*, **208**, 405 (1929).
- Schwartz, C. E., and J. M. Smith, *Ind. and Eng. Chem.*, **45**, 1209 (1953).
- Ibid.*, **51**, 1441 (1959).
- Taylor, Sir Geoffrey, *Proc. Royal Soc. London*, **219** (1953).
- Van Deemter, J. J., *Ind. and Eng. Chem.*, **45**, 1227 (1953); **46**, 2300 (1954).
- Williamson, J. E., K. E. Bazaire, and C. J. Geankoplis, *I. and E. C. Fundamentals*, **2**, 126 (1963).
- Yoshida, F., D. Ramaswami, and O. A. Hougen, *A.I.Ch.E. Journal*, **6**, 5 (1962).

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