



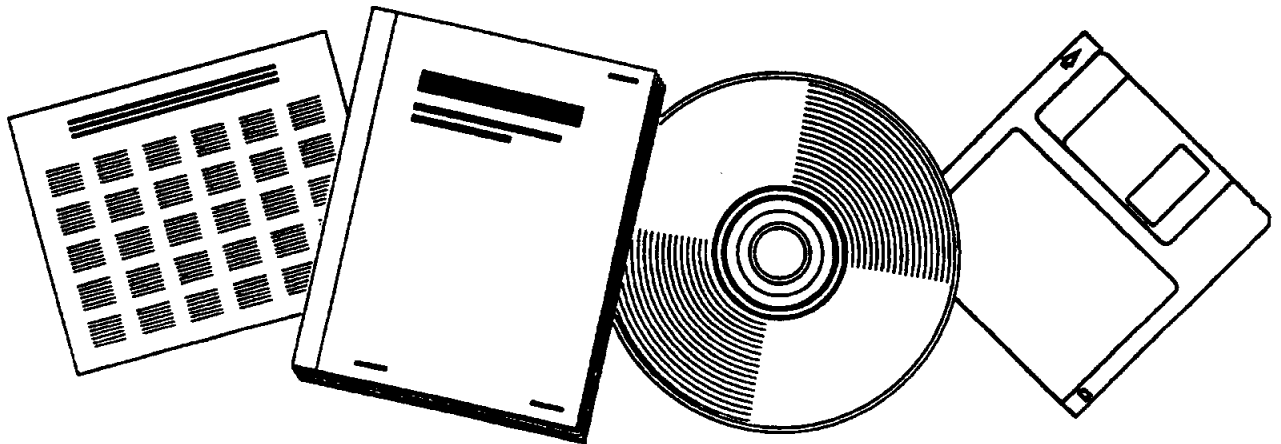
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**DIFFUSIVITIES OF SYNTHESIS GAS AND
FISCHER-TROPSCH PRODUCTS IN SLURRY MEDIA.
QUARTERLY REPORT, SEPTEMBER-DECEMBER 1984**

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DEPT. OF CHEMICAL ENGINEERING

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MEASUREMENT OF LIQUID PHASE DIFFUSION COEFFICIENTS

USING THE TAYLOR DISPERSION METHOD

Introduction

Diffusion, which is the transport of mass by random molecular motion, is a significant contribution in many rate processes. Examples of situations where liquid phase diffusion of a solute through a solvent is important are: dispersion of a pollutant through a body of water; dissolution of a solid; and migration of species to and from the surface of a catalyst during a chemical reaction. The Fischer-Tropsch process is the focus for this study.

The Fischer-Tropsch reaction is one example of a three-phase catalytic reaction in which gaseous reactants dissolve in a liquid phase, migrate to the surface of a catalyst by diffusion, and react. The products must then diffuse away from the surface to the bulk liquid. The reaction takes place at temperatures of 473 to 623 K, and pressures from 1 to 3.5 MPa. Figure 1 illustrates the sequence of steps required for the reaction to take place. It is clear that the rate of transfer of mass to and from the surface may be a key feature in determining the global reaction kinetics. The rate of mass transfer is typically characterized by an empirical mass transfer coefficient k_G , defined by

$$J = k_G(C_{Ab} - C_{Ai}) \quad (1)$$

The mass transfer coefficient in turn is typically correlated with the Schmidt number and the Reynolds number:

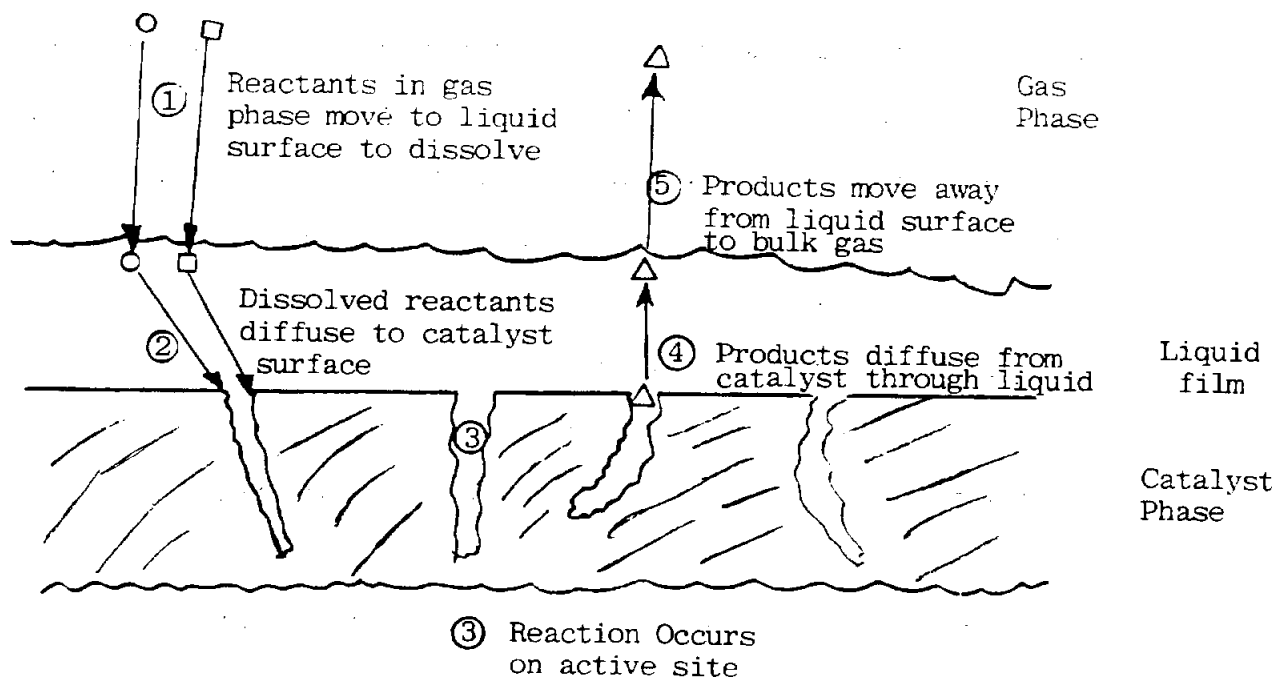


Figure 1.

Role of Mass Transfer in Kinetic Sequence in Three-Phase Catalytic Reaction

$$k_G = f(\text{Re}, \text{Sc})$$

(2)

Thus if the physical aspects (particle diameter, fluid velocity) and thermophysical properties (density, viscosity, and molecular diffusivity) are known, the mass transfer coefficient can, in principle, be calculated. However, there are severe drawbacks to this empirical approach. The main problem is that the thermophysical properties, especially the diffusivity, are seldom known with any degree of accuracy at reaction conditions; therefore, the correlations may be unreliable.

The goal of this research is to develop a fast and accurate method for measuring liquid diffusion coefficients for the Fischer-Tropsch system at temperatures from ambient to 573 K and pressures from ambient to 7 MPa. The Taylor dispersion technique will be utilized for measuring the diffusivities of carbon monoxide, hydrogen, heptane, octane, nonane, decane, and decanol in molten Fischer-Tropsch wax.

The Taylor Dispersion Experiment

Liquid diffusion is a very large field, compassing phenomena as diverse as diffusion of electrolytes in solutions and diffusion of macromolecules like proteins in blood. A multitude of techniques such as diaphragm cells, Gouy fringe measurement, optical light scattering, nuclear magnetic resonance, and chromatographic methods have been devised to handle different types of systems. The monograph of Tyrrell and Harris (1984) provides a thorough review of experimental methods of studying diffusion.

The Fischer-Tropsch system involves non-electrolytic, non-polymeric systems. In this case the Taylor dispersion technique, a chromatographic method, appears to be the most promising method. The phenomena was first reported by Griffiths (1911) who, upon injecting a pulse of colored solution into a clear tube in which water moved in laminar flow, noted that the pulse dispersed uniformly about a point moving with the mean speed of flow of the fluid. Taylor (1953, 1954) performed confirming experiments and developed the first fairly rigorous mathematical analysis which successfully predicted the phenomena. Others later extended the analysis (Aris, 1956, Hunt, 1976) and determined its limitations. Also, experimentation (Baldauf and Knapp, 1983, Pratt and Wakeham, 1975) and numerical simulation (Ananthakrishnan et al., 1965, Bailey and Grogarty, 1962) have been performed which define the conditions where Taylor dispersion holds. However, under the appropriate conditions the original development by Taylor is quite accurate. The theory as outlined in Appendix A combines the approach of Taylor (1953, 1954) and Hunt (1976). The results of the derivation are as follows. Taylor and Aris showed that dispersion of a solute pulse injected into a stream moving in laminar flow with mean velocity u_a could be described by the following differential equation:

$$K \frac{\partial^2 C_a}{\partial z^2} = \frac{dC_a}{dt} \quad (3)$$

This is the continuity equation for a disk-shaped element of radius R moving with the mean speed u_a of the laminar fluid. Here K is the

"effective dispersion coefficient" which combines the effects of diffusion and the parabolic velocity profile. K is given by

$$K = D + \frac{u_a^2 R^2}{48D} \quad (4)$$

We assume that a pulse of solute at a concentration C_a^0 is injected into a tube at time zero and position zero. The tube has approximately infinite length, with the initial and boundary conditions

$$\begin{aligned} C_a(0,0) &= C_a^0 \\ C_a(\infty,t) &= 0 \end{aligned} \quad (5)$$

For an injected pulse of finite width the solution of equation (3) is (Crank, 1956)

$$C_a = \frac{C_a^0}{2} \left[\operatorname{erf} \left(\frac{h/2 - z}{\sqrt{4Kt}} \right) + \operatorname{erf} \left(\frac{h/2 + z}{\sqrt{4Kt}} \right) \right] \quad (6)$$

For a pulse of zero width (delta input),

$$C_a = C_a^0 \left[\frac{h}{\sqrt{4\pi Kt}} \exp(-z^2/4Kt) \right] \quad (7)$$

Equation 7 describes a normal curve, which corresponds to the experimental observation that a pulse injected into a solvent flowing in laminar flow will ultimately disperse into a symmetrical plug whose center of gravity moves with the mean speed of flow. In order to use this result in measuring diffusion coefficients we must

characterize the response curve and relate the response to the parameter K , from which the molecular diffusivity D may be found. Ramachandran and Smith (1978) review several methods of response curve analysis and recommend the method of moments, which is very powerful if its limitations are considered. Radeke (1981) lists these limitations as: (1) the model used for parameter estimation should be known *a priori* to be realistic; (2) only a small number of parameters are to be estimated; and (3) data in the "tail" region of the peak should be measured very accurately since the error for higher order moments increases very rapidly in this region. For measuring the diffusivity, limitations 1 and 2 above are satisfied since the Taylor dispersion phenomena is well established theoretically and experimentally and only the first three moments are needed to determine a single parameter K . The problem of accurately measuring the peak is a function of the detector used, and indeed this is the largest source of error in using the Taylor dispersion method.

We now consider analysis of moments under the ideal conditions of the Taylor dispersion experiment. Discussion of error will be presented later in this paper. The 0th moment or sum function H corresponds to a mass balance and is given by

$$H = \int_{-\infty}^{\infty} C_a^* (Z) dZ \quad (8)$$

where C_a^* is the dimensionless concentration $(C_a - C_{ar}) / (C_a^0 - C_{ar})$. The first moment Z corresponds to the center of gravity or mean value of the peak and is given by

$$\bar{z} = \frac{1}{H} \int_{-\infty}^{\infty} z C_a^*(z) dz \quad (9)$$

The second moment σ_z^2 is the variance of the peak with respect to the mean value z :

$$\sigma_z^2 = \frac{1}{H} \int_{-\infty}^{\infty} (z - \bar{z})^2 C_a^*(z) dz \quad (10)$$

Note that all moments are defined with respect to position at a fixed instant in time. In practice, peak detection will be accomplished by passing the pulse through a detector which is fixed in position at some distance L from the injection point. The data obtained will be concentration as a function of time, and it is necessary to relate temporal moments to position moments. The 0th, 1st, and 2nd temporal moments H , \bar{t} , and σ_t^2 are defined analogously to the position moments:

$$H = \int_0^{\infty} C_a^*(t) dt \quad (11)$$

$$\bar{t} = \frac{1}{H} \int_0^{\infty} t C_a^*(t) dt \quad (12)$$

$$\sigma_t^2 = \frac{1}{H} \int_0^{\infty} (t - \bar{t})^2 C_a^*(t) dt \quad (13)$$

Then for a pulse injection, the temporal and position moments are related as follows (Van der Laan, 1958, Pratt and Wakeham, 1974, Levenspiel and Smith, 1957):

$$\bar{t} = (L/u_a) [1 + \sigma_z^2/u_a^2 Lt] \quad (14)$$

$$\sigma_t^2 = \left(\frac{L}{u_a}\right)^2 \left[\sigma_z^2 / u_a L t + 2\sigma_z^4 / (u_a L t)^2 \right] \quad (15)$$

Aris (1956) calculated the variance of the distribution of a square pulse injection:

$$\sigma_z^2 = \sigma_z^2(t=0) + 2Kt - 128 \frac{u_a^2 R^4}{D^2} \times \sum \lambda_n^{-8} [1 - \exp(-\lambda_n^2 \frac{Dt}{R^2})] \quad (16)$$

λ_n is the n^{th} root of the Bessel function of the first kind of order zero, J_0 . Under the appropriate conditions, the last term of equation (16) is negligible. In addition, equations (14) and (15) may be simplified under ideal conditions to give

$$\bar{t} = L/u_a = \bar{t}_L \quad (17)$$

and

$$\sigma_t^2 / \bar{t}^2 = \sigma_z^2 / L^2 \quad (18)$$

so that ultimately the diffusivity may be calculated from the equation

$$D = u_a R^2 / 48K = R^2 \bar{t}_L / 24\sigma_t^2 \quad (19)$$

In summary, Taylor dispersion is described to a very good approximation by the differential equation (3). The parameter K given by (4) combines the effects of bulk laminar flow and molecular diffusion which causes the solute to disperse. The solutions to (3) for a delta injection or a finite pulse injection are equations (7) and (6), respectively. The variance of the resulting normal curve is

related to K by equation (16). Data is obtained as concentration versus time, and the first temporal three moments are calculated from equations (11) - (13). Then, for ideal conditions, the equation for determining the diffusivity D is given by (19).

In the next section we will describe an apparatus for measuring the diffusivities at elevated temperature and pressure using the Taylor dispersion technique. The criteria for the analysis to hold will be given, along with a discussion of practical aspects of the experiment which will lead to departures from the ideal analysis.

Apparatus Design

In accordance with the above discussion, the essential elements of the apparatus are: (1) injection of a short, square pulse into a stream in laminar flow; (2) a long smooth tube of circular cross section in which dispersion occurs; (3) detection of the solvent peak with minimum disturbance of the peak; and (4) maintaining very precisely temperatures and pressures up to 623 K and 7 MPa. An excellent and thorough discussion of the criteria for constructing a Taylor dispersion apparatus at moderate temperatures and pressures (243 K and 0.1 MPa) was given by Alizadeh et al. (1980).

To maintain laminar flow, we require

$$Re = 2u_a R \rho / \mu < 2300 \quad (20)$$

To insure that axial diffusion contributes less than 0.01 % to the second moment of the distribution, we require

$$u_a > 700 D/R \quad (21)$$

To insure that the equations for the second moment can be written in a simple, closed form, we require

$$DL/u_a R^2 = Dt/R^2 > 10 \quad (22)$$

In a practical apparatus it is necessary to coil the diffusion tube so it can be placed in a thermostatic bath. To insure that secondary flows resulting from flow in a coil contribute no more than 0.05% to the second moment, we require

$$\bar{t} = L/u_a > \frac{1}{5} \frac{R^3 L^2 f}{D \mu R_c} \quad (23)$$

When conditions (20) through (23) are met, then an equation for the diffusivity, accurate to about 0.5%, is

$$D = \frac{R^2}{24 \bar{t}_{ID}} \frac{[1 + 4 \sigma_{ID}^2 / \bar{t}_{ID}^2]^{1/2} + 3}{[1 + 4 \sigma_{ID}^2 / \bar{t}_{ID}^2]^{1/2} + 2 (\sigma_{ID}^2 / \bar{t}_{ID}^2) - 1} \times \left[\frac{1}{2} + \frac{1}{2} (1 - \delta_a)^{1/2} \right]$$

$$\delta_a = 12.7997 \epsilon_0 \quad (24)$$

$$\epsilon_0 = \frac{2\sigma_{ID}^2 - \bar{t}_{ID}^2 + \{\bar{t}_{ID}^2 + 4\bar{t}_{ID}^2 \sigma_{ID}^2\}^{1/2}}{(8\bar{t}_{ID}^2 - 4\sigma_{ID}^2)}$$

Here t_{ID} and σ_{ID}^2 are the first and second temporal moments which would be obtained from an apparatus with no deviations from Taylor's theory. These ideal quantities are related to the actual experimental moments t_{exp} and σ_{exp}^2 by

$$\begin{aligned}\bar{t}_{ID} &= \bar{t}_{exp} + \Sigma \delta\bar{t}_i \\ \sigma_{ID}^2 &= \sigma_{exp}^2 + \Sigma \delta\sigma_i^2\end{aligned}\tag{25}$$

The corrections δt_i and $\delta \sigma_i^2$ were developed by Alizadeh et al. (1980) to account for the following imperfections which will be present in a real apparatus: (1) a finite volume of the detection monitor; (2) a finite injection volume; (3) a length of connecting tube between the diffusion tube and the detector monitor. These corrections are given in Appendix B.

Alizadeh et al. (1980) also show how to eliminate two other possible imperfections in the equipment. The internal diameter of the tube should be determined by measuring the volume of a fluid it contains, rather than by relying on the nominal tube i.d. for the calculation. Then any non-uniformities in cross-sectional area will have negligible effect on the calculations. Another possible deviation from ideality is a non-circular (elliptical) tube cross-section. Alizadeh et al. (1980) show that if the cross-section is elliptical with major and minor semiaxes a_1 and a_2 , the effect on D is less than 0.7% if the ratio a_1/a_2 is greater than 0.866.

It remains to apply these design criteria using typical or expected values of fluid and equipment properties to design the

Taylor dispersion apparatus. For the normal alkane systems of interest in this study, some typical ranges of physical and thermophysical properties are shown in Table 1. Diffusivities are based on those measured by Alizadeh and Wakeham (1982) for hexane, heptane, and octane binary mixtures. For the heavy solvents (C_{20} and heavier) typical of Fischer Tropsch mixtures, we expect diffusivities to be about the same or smaller than theirs. The viscosity values shown were calculated from correlations of Reid et al. (1977), for temperatures up to about 423 K. We note that the temperature dependence of viscosity is much stronger than that of the density or diffusivity. We assume for design purposes that the density is approximately constant.

Table 1

Approximate Thermophysical Properties of Alkanes used for
Design of Apparatus

Density, kg/m^3	780
Viscosity, $kg/m-s$	$0.2 \text{ to } 5 \times 10^{-3}$
Diffusivity, m^2/s	$0.1 \text{ to } 5 \times 10^{-9}$

To meet criterion (22), the diffusion tube radius R is on the order of 0.5×10^{-3} m. A commercially available tubing is 1.5875 $\times 10^{-3}$ m o.d. stainless steel with a nominal i.d. of 5.08×10^{-4} m. To keep the size of the apparatus within feasible limits, we assume an upper bound of 0.3048 m on the diameter for coiling the diffusion

tube. If we regard these dimensions as fixed, then we are left with specifying diffusion tube length L from the given criteria, and average velocity u_a (or the volumetric flow rate Q) from criteria (21) and (23). These last two criteria may conflict, for they describe the upper and lower bounds on u_a .

If we solve both (21) and (23) for u_a we get

$$\frac{700D}{R} < u_a < \frac{5D\mu R_c}{R^3 \rho} \quad (26)$$

Figure 2 is a plot of this equation with D , R , R_c , and ρ fixed. The viscosity is the independent variable and now we see from (26) how the large decrease in viscosity will cause a pinch in u_a . The result is that at low viscosity, Reynolds number will increase and the secondary flow effects begin to contribute more than 0.05%. Practically speaking, if the viscosity drops appreciably below about 1×10^{-2} kg/m-s, neither R nor R_c can be adjusted sufficiently to prevent secondary flow effects. Therefore at this value of viscosity or below, we expect to see small effects in the diffusivity measurement resulting from coiling the tube. It will be necessary to check the results from each measurement for effects of coiling the tube. This may be done by repeating the measurement at different flow rates.

The maximum value of u_a from Figure 2 is on the order of 0.013 m/s. Using criteria (22), with $R=5.08 \times 10^{-4}$ m and $D=2.2 \times 10^{-4}$ m, we get a minimum value of L as 15.2 m. Tentative specifications for the apparatus, based on the above discussion, are given in Table 2.

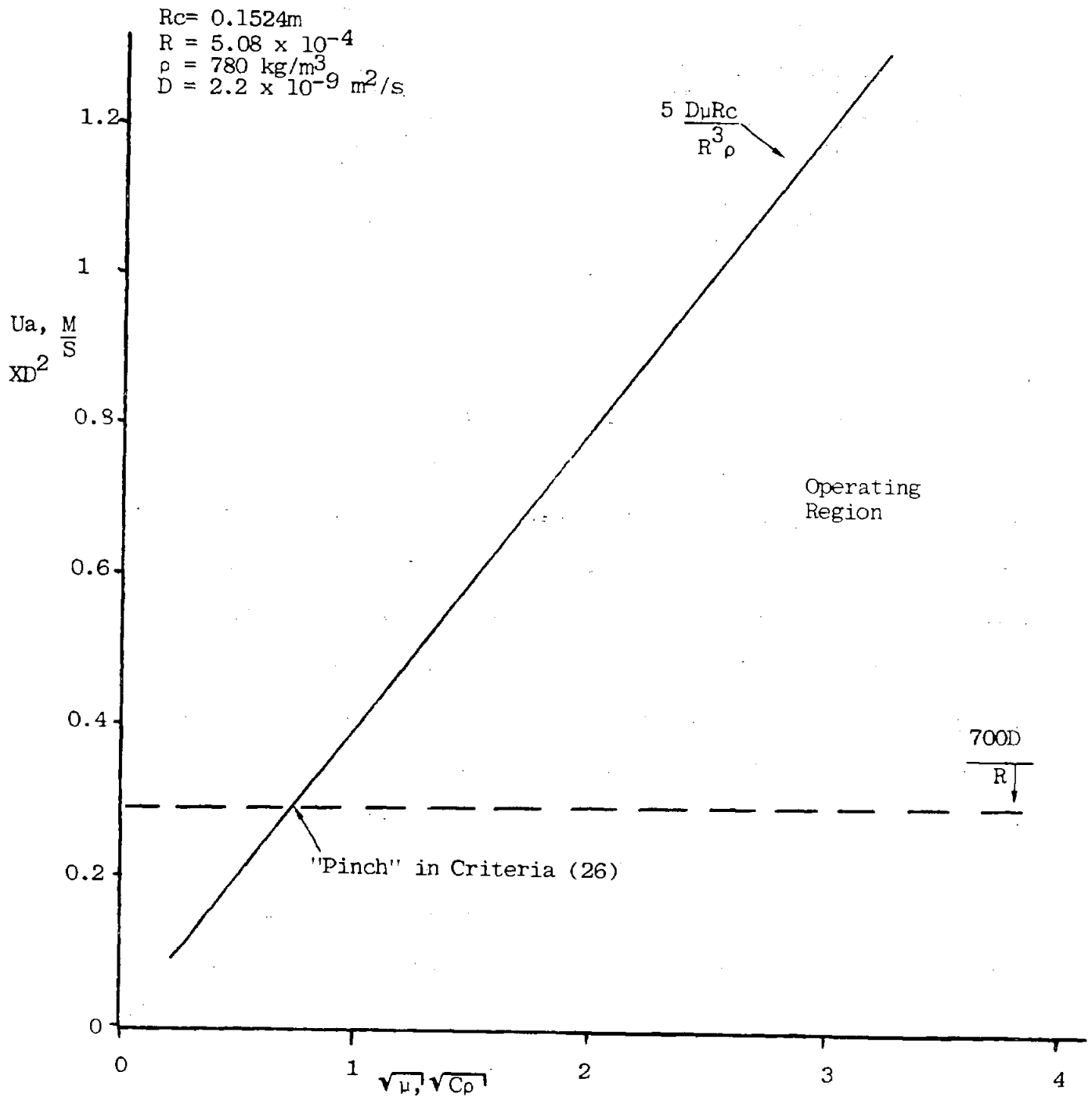


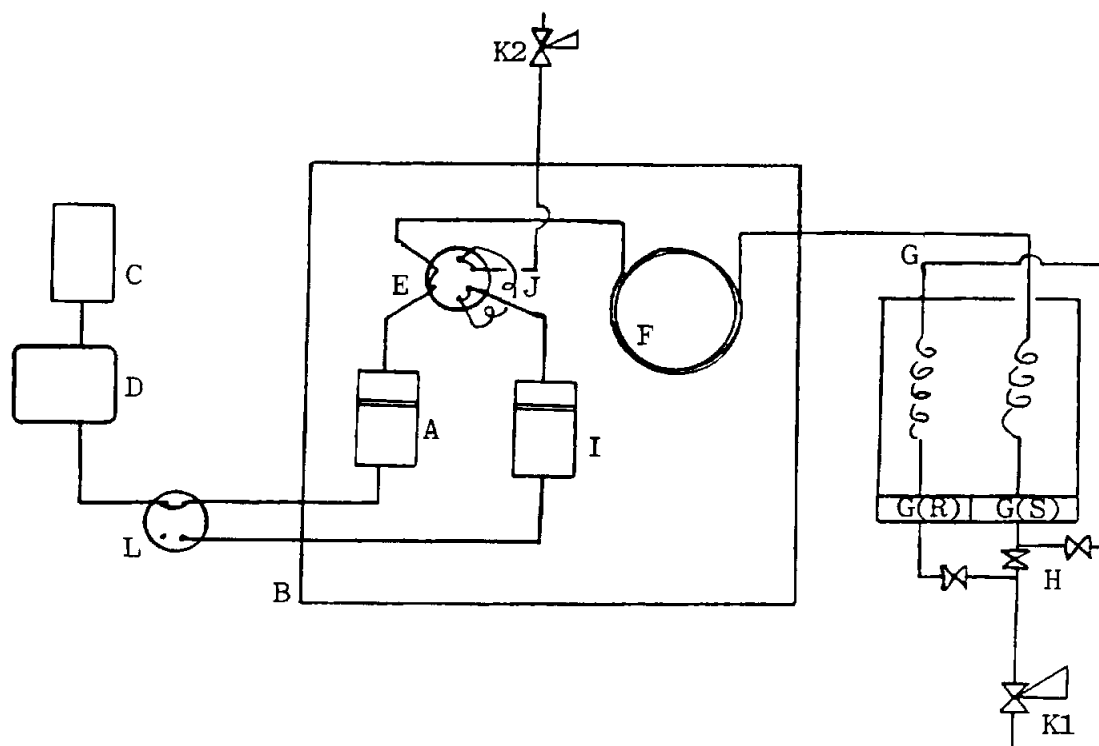
Figure 2.
 Plot of Criteria (26) Demonstrating Conflict at Low Viscosity

Table 2

Tentative Equipment Specifications

Diffusion Tube Length, m	40
Diffusion tube i.d., m	5.08×10^{-4}
Radius of coiled tube, m	0.1524
Maximum flow rate, m ³ /min	0.6×10^{-6}
Volume of piston pump, m ³	4×10^{-4}
i.d. of piston pump, m	0.0762
Stroke length of piston pump, m	0.087
Detector volume, m ³	8×10^{-9}
Injection volume, m ³	$<100 \times 10^{-9}$

Figure 3 shows a diagram of the proposed apparatus. The objectives are to eliminate deviations from the theoretical model, to design so that unavoidable deviations can be calculated, and to build a rugged apparatus which can be automated. Thus, rapid accumulation of good diffusivity data can be achieved. The pure solvent will be placed on one side of a piston A and enclosed in a thermostatic enclosure B, which can be maintained at temperatures up to 573 K. An inert fluid, such as Dowtherm or a glycerin oil, will be used to drive the piston. This fluid will be pumped from an ambient reservoir C through a precision metering pump D. This arrangement for pumping the solvent is used to avoid the difficulties involved in heating the precision metering pump. The pure solvent flows through one side of the 6-port switching valve E, through the coiled diffusion tube F, and then out of the thermostatic enclosure to the detector G. The detector we plan to begin with is a refractive index detector. It is common to fill the reference side of the detector with fluid and let it remain



- A. Solvent piston
- B. Thermostatic enclosure
- C. Inert fluid reservoir
- D. Precision metering pump
- E. 6-port switching valve
- F. Coiled diffusion tube
- G. RI detector
- H. Valve manifold
- I. Sample fluid piston
- J. Sample loop

- K1. Backpressure regulator
- K2. Backpressure regulator
- L. Switching valve

Figure 3
Schematic of Taylor Dispersion Apparatus.

stagnant; therefore we plan to build the valve manifold H around the detector so that fluid can be pumped through the sample side G(s) and then around to fill the reference side G(r). After filling and pressuring both sides of the cell, the reference side will be isolated from the flowing sample side by appropriate valving. The pressure will be controlled by back pressure regulator K1. This arrangement saves solvent and eliminates the cost of an independent pump for the reference side. Baseline shift will help notify us as to possible leaks or degradation of solvent on the reference side.

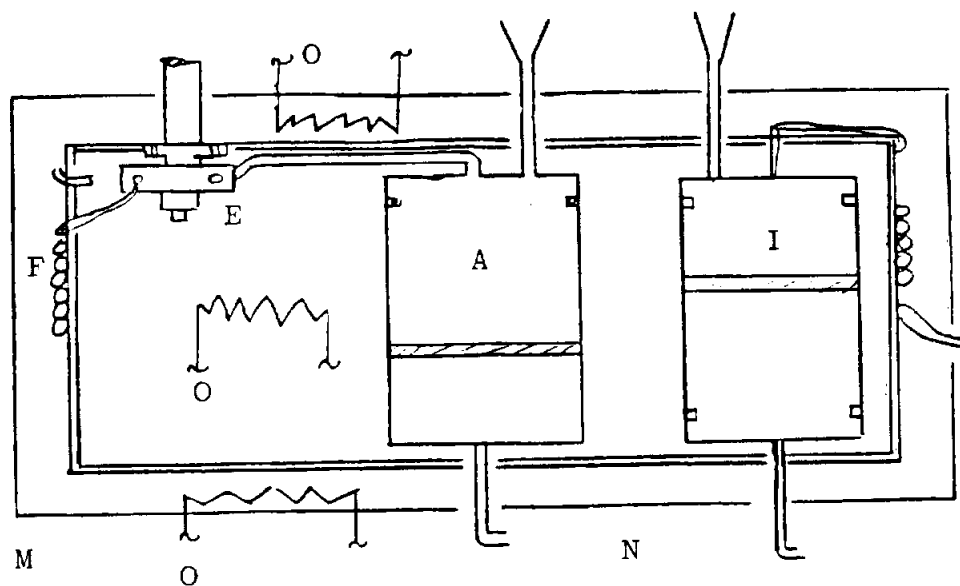
The sample fluid (solvent containing the desired amount of solute) will be prepared and placed in another piston I, contained within the thermostatic enclosure. Through the same means of pumping an inert fluid, sample fluid will be pumped into the sample loop J on the 6-port sampling valve E. A back pressure regulator K2 on the outlet of the sample loop can be set so that the sample fluid is at the same pressure as the fluid in the diffusion tube. Continuous flow through the sample loop is not necessary; however, it will be necessary to flush and refill the sample loop after each injection into the diffusion tube. Thus, another switching valve L is installed so that the inert fluid can be diverted momentarily from piston A to piston I. The sequence of events from start up will thus be as follows:

- (1) Fill piston A with reference solvent and piston I with solvent/ solute mixture.
- (2) Allow enclosure B to come to desired temperature.

- (3) Set switching valves L and E to pump reference fluid through the diffusion tube coil and then to the detector. Fill both sides of the detector with reference fluid at a pressure controlled by the back pressure regulator K1.
- (4) Isolate the reference side of the detector.
- (5) Use valve L to divert inert fluid to piston I. Fill the sample loop J, then divert flow back to piston A.
- (6) Use switching valve E to inject the desired amount of solute from the sample loop, then switch back to the original position.
- (7) The sample will disperse through coil F, and a peak will be recorded.
- (8) When the peak has completely passed the detector, return to step (4). Repetitions can be obtained until there is no more liquid left in the pistons.

A microprocessor and interfaces can be used to control the pump and switching valves, and also to record data from the detector. Thus the process, except for start up steps (1) through (4), can be automated to provide repetitive measures of diffusivity. It may be desirable to change flow rates or sample injection volume between measurements, and this too can be easily accomplished via computer control.

We now give more detailed description of the key features of the apparatus. Figure 4 is a cross section of the physical layout of



- A. Solvent piston
- E. 6-port switching valve
- F. Coiled diffusion tube
- I. Sample fluid piston
- M. Aluminum enclosure
- N. Insulation
- O. Heaters

Figure 4
Cross-Section of Thermostatic Enclosure

the thermostatic enclosure. It contains the piston pumps A and I, switching valve E, and diffusion coil F. (Letters refer to both Figures 3 and 4.) The pumps and valve will be mounted within a aluminum enclosure M. The enclosure will be cylindrical with a radius of 0.1524 m and an height of 0.15 to 0.25 m. The diffusion tube will be coiled around the enclosure. The design will allow all metal parts to come in good contact with the aluminum enclosure, providing thermal mass and good conductive heat transfer for temperature stability and control. The aluminum enclosure will be wrapped with insulation N. Electric heaters O of various wattage will be placed in and around the aluminum enclosure as necessary to achieve the desired temperature. The inside will be filled with lead or copper shot to increase thermal mass and conductive heat transfer.

The detector we are considering is a LDC/Milton Roy Refractomonitor III. It has a detector cell with built-in heat exchanger, which we will heat independently of the thermostatic enclosure. Refractive index is very sensitive to temperature fluctuations, thus the built-in heat exchanger. Also, heating the detector cell will be necessary to keep heavy wax solvents from freezing in the detector. This particular model shows most promise among commercial detectors of being able to withstand pressures up to 7 MPa. To achieve temperatures of up to 423 K in the detector it may be necessary to replace the standard Teflon gaskets with some other material. (There are no commercially available RI detectors

which could be placed into the thermostatic enclosure.) Heating will be accomplished by circulating Dowtherm A through the cell heat exchanger from a recirculating heating bath. The heat exchanger is simply an enclosure filled with heating fluid. Sample and reference fluid lines are coiled in the exchanger to insure enough time for temperature equilibration. (Coiling of the sample line will affect the measured peak response. The magnitude of the effect will be estimated from the dimensions of the detector cell and the properties of the particular sample being tested.)

The solvent pump we are considering is a LDC/Milton Roy Constametric III with purge valve and slow speed option. Its capacity is 0.03 to 3.33 ml/minute at output pressure up to 40 MPa. It has independent high and low pressure shut down logic and is computer controllable. The automatic high/low pressure shutdown feature is a key safety item for automated operation.

The six-port sample injection valve is a Valco Instruments model capable of 10 MPa and 573 K. We plan to purchase the pneumatically driven switching option because this allows the valve to change positions in less than 10 milliseconds (Harvey and Stearns, 1984). Thus the sample can be injected with negligible interruption of flow caused by valve switching. The volume injected can also be precisely controlled by controlling the time spent in the "inject" position. The appropriate electronic interface with the pneumatic driver makes this valve computer controllable, as well.

The two piston pumps will be machined in our Chemical Engineering Thermodynamics laboratories. Our thermodynamics personnel have extensive experience with precision machining and have built these kinds of pumps in the past. The pump is simply a smooth bore cylinder with a piston and gaskets to separate the driving fluid from the sample fluid. Leak prevention across the piston is relatively easy, since the pressure difference across the piston is small (just large enough to overcome the friction along the walls of the piston pump).

We have not yet decided on the microprocessor we will use to automate the equipment and record data. We are currently leaning toward a Hewlett-Packard 9600S. This machine would be compatible with the Hewlett-Packard minicomputer which the Chemical Engineering Department is purchasing for general computing purposes. Also, the 9600 is designed for on-line control, data acquisition, and calculations. It would easily handle the tasks described in this report and allow for additional duties, as well.

Status of Purchasing and Budget

The approximate total cost of the metering pump, RI detector, switching valves, pressure regulators, strip chart recorder, and the HP 9600S is in the neighborhood of \$16,000. The budgeted amount for special equipment was \$21,000, thus leaving an estimated \$5,000 for purchasing the material for the constant temperature environment, piston pumps, pressure measuring equipment, temperature measurement, and other control instruments. We are currently seeking competitive

bids, through the Research Foundation staff, for the detector, pump, and switching valves. Investigation into the most appropriate microprocessor is still continuing. We anticipate purchase orders for the major equipment items being placed shortly.

Conclusions

The theoretical criteria for measuring diffusivities by the Taylor dispersion method have been given. In addition, the practical departures from an ideal experiment have been discussed; correction for the non-ideal conditions are found in Appendix B (Alizadeh et al., 1980). The effect of varying viscosity on secondary flow effects has been pointed out; it appears that under typical laboratory space limitations, using commercially available tubing, and with diffusivities on the order of 10^{-9} m²/s, it will not be possible to completely eliminate these effects. An apparatus for measuring diffusivity at high temperatures and pressures, where data has heretofore been scarce, is presented. With this apparatus rapid measurements may be made, and with the aid of computer control the measurements may be repeated and large volumes of data generated with minimum requirements of the operator. We anticipate our accuracy being between 0.5 and 4%.

LITERATURE CITED

- Alizadeh, A.A. and W.A. Wakeham, "Mutual Diffusion Coefficients for Binary Mixtures of Normal Alkanes," *Int. J. Thermophysics*, 3, 307 (1982).
- Alizadeh, A., C.A. Nieto de Castro, and W.A. Wakeham, "The Theory of the Taylor Dispersion Technique for Liquid Diffusivity Measurements," *Int. J. Thermophysics*, 1, 243 (1980).
- Ananthakrishnan, V., W.N. Gill, and Allen J. Barduhn, "Laminar Dispersion in Capillaries: Part I. Mathematical Analysis," *A. I. Ch. E. J.*, 11 (6), 1063 (1965).
- Aris, R., "On the dispersion of a solute in a fluid flowing in a tube," *Proc. Roy. Soc. A*, 235, 67 (1956).
- Baldauf, W., and H. Knapp, "Measurement of Diffusivities in Liquids by the Dispersion Method," *Chem. Eng. Sci.*, 38 (7), 1031 (1983).
- Bailey, H.R. and W.B. Grogarty, "Numerical and experimental results on the dispersion of a solute in a fluid in laminar flow through a tube," *Proc. Roy. Soc. A*, 269, 352 (1962).
- Bird, R.B., W.E. Stewart, and E.N. Lightfoot, "Transport Phenomena," John Wiley and Sons, N.Y. (1960).
- Crank, J., "The Mathematics of Diffusion," Clarendon Press, Oxford (1956).
- Gill, W.N., "A note on the solution of transient dispersion problems," *Proc. Roy. Soc. A*, 289, 335 (1967).
- Griffiths, A., "Movement of a Coloured Index along a Capillary Tube and its Application to the Measurement of the Circulation of Water in a Closed Circuit," *Proc. Phys. Soc.*, 23, 190 (1911).
- Harvey, M.C. and S.D. Stearns, "High-Speed Switching of Liquid Chromatographic Injection Valves," *Analytical Chem.*, 56, 837 (1984).
- Hunt, B., "Diffusion in Laminar Pipe Flow," *Int. J. Heat Mass Trans.*, 20, 393 (1976).
- Levenspiel, O. and W.K. Smith, "Notes on the diffusion-type model for the longitudinal mixing and flow," *Chem. Eng. Sci.*, 6, 227 (1957).
- Pratt, K.C. and W.C. Wakeham, "The mutual diffusion coefficient for binary mixtures of water and the isomers of isopropanol," *Proc. Roy. Soc. A*, 342, 401 (1975).

- Radeke, K. H., "Critical Remarks on Using Moments Method," *I. E. C., Fund.*, 20, 302 (1981).
- Ramachandran, P.A. and J.M. Smith, "Transport Rates by Moment Analysis of Dynamic Data," *I. E. C., Fund.*, 17, 148 (1978).
- Taylor, G., "Dispersion of soluble matter in solvent flowing slowly through a tube," *Proc. Roy. Soc. A*, 219, 186 (1953).
- Taylor, G., "Conditions under which dispersion of a solute in a stream of solvent can be used to measure molecular diffusion," *Proc. Roy. Soc. A*, 225, 473 (1954).
- Tyrrell, H.J.V. and K.R. Harris, "Diffusion in Liquids," Chapter 5, Butterworths, London (1984).
- Van der Laan, E. Th., Letter to editor, *Chem. Eng. Sci.*, 7, 187 (1958).

NOMENCLATURE

C	Concentration
C_a	Concentration averaged over tube cross-section
C_{a0}	Average concentration in injected pulse
C_{Ai}	Interface concentration of component A
C_{Ab}	Bulk concentration of component A
C_{ar}	Concentration of solute in reference stream
C_a^*	Reduced concentration $(C_a - C_{ar}) / (C_a^0 - C_{ar})$
D	Diffusivity
H	0th position moment
h	Width of injected pulse
K	Effective dispersion coefficient
k_G	Mass transfer coefficient
L	Length of diffusion tube
j	Molar flux
R	Tube radius
R_c	Radius of coiled tube
Re	Reynolds number
Sc	Schmidt number
t	1st temporal moment
t_{ID}	1st temporal moment for an ideal experiment
t_{exp}	1st temporal moment for an actual experiment
t_L	Time from injection to passing of peak maximum through detector
V_D	Detector volume
V_i	Volume of sample injected

u_a Mean velocity in tube
 Z Coordinate moving with mean speed of flow; see equation (A8)
 Z 1st position moment
 μ viscosity
 ρ density
 σ_z^2 2nd position moment
 σ_t^2 2nd temporal moment
 δt_i Correction to 1st moment for non-ideality in equipment
 $\delta \sigma_i^2$ Correction to 2nd moment for non-ideality in equipment

APPENDIX A

Derivation of Taylor Dispersion Theory

The continuity equation for a species in terms of its molar concentration C , at a fixed point (r, z) , may be written in cylindrical coordinates:

$$D \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C}{\partial r} \right) + \frac{\partial^2 C}{\partial z^2} \right] = u_a \left[1 - \left(\frac{r}{R} \right)^2 \right] \frac{\partial C}{\partial z} + \frac{\partial C}{\partial t} \quad (\text{A1})$$

Here the diffusivity D is assumed constant, and the fluid is in laminar flow with the familiar parabolic velocity profile

$$u(r) = u_a \left[1 - \left(\frac{r}{R} \right)^2 \right] \quad (\text{A2})$$

Since we measure concentration as averaged across the tube cross section and not a point value as in equation (A1), we define the average concentration by

$$C_a = \frac{2}{R^2} \int_0^R C(r) r \, dr \quad (\text{A3})$$

If we multiply equation (A1) by $2r/R^2$ and integrate from 0 to R , we obtain the averaged continuity equation:

$$D \frac{\partial^2 C_a}{\partial z^2} + \frac{4u_a}{R^4} \frac{d}{dz} \int_0^R (C - C_a) r^3 dr = \frac{\partial C_a}{\partial t} + u_a \frac{\partial C_a}{\partial z} \quad (\text{A4})$$

Taylor assumed that the experiment could be performed under conditions where radial concentration gradients, caused by the axial flow profile, would be rapidly damped out by radial diffusion. Under such conditions he showed (Taylor, 1954) that

$$(C-C_a) = \frac{R^2 u_a}{4D} \frac{\partial C_a}{\partial z} \left[-\frac{1}{3} + \left(\frac{r}{R}\right)^2 - \frac{1}{2} \left(\frac{r}{R}\right)^4 \right] \quad (\text{A5})$$

When equation (A5) is substituted into equation (A4), and the integration performed, we obtain directly

$$K \frac{\partial^2 C_a}{\partial z^2} = u_a \frac{\partial C_a}{\partial z} + \frac{\partial C_a}{\partial t} \quad (\text{A6})$$

where

$$K = D + \frac{u_a^2 R^2}{48D} \quad (\text{A7})$$

Now equation (A6) shows the continuity equation in terms of concentration at a fixed point z as averaged across the tube cross section. The time derivative is with respect to a stationary point, and K is the effective dispersion coefficient. (Dispersion in henceforth used to describe spreading of a solute pulse by any combination of mechanisms, whereas diffusion refers strictly to random molecular motion, with no convective or bulk flow contribution.) Since we observe experimentally that the peak disperses about a point moving with the mean speed of the fluid, we want to rewrite the derivative terms accordingly. We define a coordinate Z ,

$$Z = z - u_a t \quad (\text{A8})$$

and note that, for t held constant,

$$\frac{\partial}{\partial Z} = \frac{\partial}{\partial z} ; \quad \frac{\partial^2}{\partial Z^2} = \frac{\partial^2}{\partial z^2}$$

We also make use of the total time derivative, which describes the time rate of change as measured by an observer moving at a given velocity. From Bird et al. (1960), the total time derivative d/dt is

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \frac{\partial}{\partial z} \frac{\partial z}{\partial t} \quad (\text{A9})$$

where dz/dt is in our case simply the velocity u_a . Substituting for the derivatives in equation (A6), we get

$$k \frac{\partial^2 C_a}{\partial z^2} = \frac{dC_a}{dt} \quad (\text{A10})$$

which is the continuity equation for a disk-shaped element of radius R moving with the mean speed u_a of the laminar fluid.

APPENDIX B

Corrections for Non-Idealities in the Taylor Dispersion Experiment

The following corrections for a practical Taylor dispersion experiment were developed by Alizadeh et al. (1980). When the detector at the end of the diffusion tube has a finite volume V_D which acts as a perfectly mixed chamber, the corrections to t_{ID} and σ_{ID}^2 are given by

$$\delta \bar{t}_1 = \left(\frac{L}{u_a} \right) \left[3\xi_0 - \frac{V_D}{\pi R^2 L} \right] \quad (B1)$$

$$\delta \sigma_1^2 = \left(\frac{L}{u_a} \right)^2 \left[13\xi_0^2 - \left(\frac{V_D}{\pi R^2 L} \right)^2 - 2\xi_0 \left(\frac{V_D}{\pi R^2 L} \right) \right]$$

For a finite injection volume V_i , the corrections are

$$\delta \bar{t}_2 = - \left(\frac{L}{u_a} \right) \left(\frac{V_i}{2\pi R^2 L} \right) \quad (B2)$$

$$\delta \sigma_2^2 = \frac{-1}{12} \left(\frac{L}{R} \right)^2 \left(\frac{V_i}{\pi R^2 L} \right)^2$$

For a length of connecting tube of radius R_{ct} and length l between the diffusion tube and the detector, the corrections are

$$\delta \bar{t}_3 = \frac{1}{u_a} \left(\frac{R_{ct}}{R} \right)^2 \left[1 + \frac{R^2}{R_{ct}^2} \left(\frac{L}{l} \right) \xi_0 \left(1 + \frac{R_{ct}^2}{R^2} \right) \right]$$

$$\delta \sigma_4^2 = \left(\frac{l}{u_a} \right)^2 \left(\frac{R_{ct}}{R} \right)^2 \left[2 \frac{R^2}{R_{ct}^2} \left(\frac{L}{l} \right) \xi_0 + \frac{R^2}{R_{ct}^2} \left(\frac{L}{l} \right)^2 \xi_0^2 \left(\frac{3R_{ct}^2}{R^2} + 2 \right) \right] \quad (B3)$$

The corrections are said to amount to no more than 0.5% in any case, therefore the corrections can be made by first calculating the moments as if the experiment were ideal, then calculating the corrections from equations B1-B3. Then the diffusivity is calculated from equations (24) and (25).