

The Theory of the Taylor Dispersion Technique for Liquid Diffusivity Measurements

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This paper presents a complete analysis of the theory of an instrument to measure the diffusion coefficients in liquid mixtures based upon the phenomenon of Taylor dispersion. The analysis demonstrates that it is possible to design an instrument that operates very nearly in accordance with the simplest mathematical description of the dispersion of a solute pulse in a fluid in laminar flow within a straight, circular cross-section tube. The small departures of a practical instrument from the ideal are evaluated as corrections by means of a general perturbation treatment that allows them to be examined one at a time. The corrections considered include the effects of the finite volume of the injection pulse, the finite volume of the concentration monitor, the coiling of the tube, and the nonuniformity and noncircularity of the cross section, as well as the variation of the fluid properties with composition. All the equations necessary for the design of an instrument of this type, and for the evaluation of experimental data free from significant systematic errors, are presented.

KEY WORDS: diffusion coefficient; liquid mixtures; Taylor dispersion; liquid diffusion.

1. INTRODUCTION

The process of molecular diffusion in liquids is often the rate limiting factor in chemical engineering operations involving mass transfer such as absorption, liquid-liquid extraction, and heterogeneous chemical reactions (1). More-

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over, the diffusion coefficient is that liquid phase transport property most easily calculated in molecular dynamics simulations, which are valuable tools in the development of theories of the liquid state [2]. It is therefore regrettable that there have been few accurate, systematic studies of molecular diffusion coefficients in the liquid phase. The principle reason for these lack of measurements is undoubtedly the inherent slowness of the diffusion process in liquids, which necessitates experiments of several days' duration to obtain a single datum.

For particular systems, special techniques have now been developed that permit rapid measurement of diffusion coefficients with moderate accuracy. For example, the self-diffusion coefficients of macromolecules in dilute solutions may now be studied by photon-correlation spectroscopy [3]. For simpler liquid systems, two more generally applicable techniques have recently been developed, which promise both rapid diffusivity determinations and relatively high accuracy. The first method is one based upon holographic interferometry [4, 5]. In this technique, the concentration changes arising from diffusion in a static liquid mixture of initially nonuniform composition are followed using optical interference techniques and interpreted with the aid of Fick's Law of Diffusion. Because of the high resolution associated with the optical method of observation, this experimental technique is probably the most accurate available [4]. However, the method is restricted to the measurement of mutual, or interdiffusion, coefficients in liquid mixtures.

The second method, which has sometimes been called the chromatographic broadening technique [4], is based upon the work of G. I. Taylor, published in 1953, in which he analyzed the dispersion of a pulse of soluble material in a solvent flowing in laminar flow through a circular section tube [6]. In essence, the experimental technique makes use of the velocity profile characteristic of laminar flow to enhance the dispersion of the pulse brought about by molecular diffusion alone. The coupling of the flow-induced dispersion with molecular diffusion in this way has the result that a significant dispersion of an initially concentrated pulse can be achieved in a short time. Furthermore, the flow of the fluid allows a single concentration monitor fixed at one point in space to observe all of the dispersed solute, instead of the spatially distributed measurements of concentration necessary in other methods. The technique therefore has the virtues of rapidity and simplicity, and it has been employed for several independent sets of measurements [7–12].

However, the theoretical description of the dispersion process given originally by Taylor, and later more exactly by Aris [13], was not intended to form the foundation of a technique for diffusivity measurements, but rather to predict solute dispersion in pipelines. Consequently, the use of this theoretical description of the dispersion process without modification for the particular application of diffusivity measurements has, in the past, been

justified on the basis of empirical observations. Such procedures inevitably degrade the accuracy of the experimental data obtained, and for this reason, the method has been termed one of moderate accuracy [4]. In this paper, we provide a more complete treatment of the theory of the Taylor dispersion method for diffusivity measurements in order to obtain a set of working equations for an instrument operating on this principle. In turn, these equations permit us to assess the accuracy of the results of measurements with this method, and to show that it can be made comparable with that of other techniques. In a companion paper, measurements of liquid phase diffusion coefficients are reported that support this contention.

2. THE PRINCIPLE OF THE EXPERIMENTAL METHOD

We consider first the simplest mathematical model of an instrument to measure liquid phase diffusivities using Taylor dispersion. This mathematical model refers to an idealized experiment, which cannot be realized in practice. Nevertheless, it will be shown that a practical instrument can be designed so that its departures from the ideal are small and so that they may be evaluated with the aid of a proper analysis.

Figure 1 shows the ideal experimental arrangement and defines the geometry of the apparatus. For generality, we consider a homogeneous liquid mixture of species 1 and 2 flowing in laminar flow through an infinitely long, isothermal, straight tube of uniform, circular cross section, radius a_0 , with impermeable walls. We denote the molar concentrations of the species in the flowing mixture by C_{1f} and C_{2f} , respectively. The mean velocity of the liquid mixture in the tube is denoted by \bar{u}_0 . At time $t = 0$, a sample of liquid mixture of the same two components of a different composition is introduced into the tube at $z = 0$. The molar concentrations of the two components in the sample are C_{1i} and C_{2i} , respectively, and its mass density is supposed the same as that of the flowing stream. The sample fills the cross section of the tube at $z = 0$

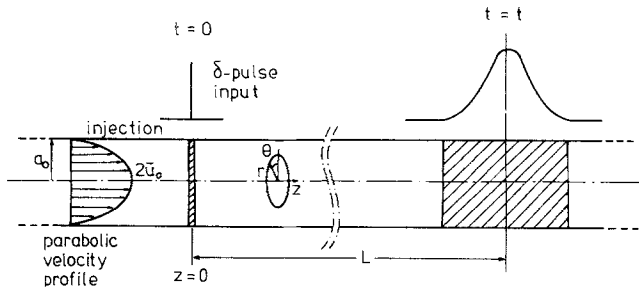


Fig. 1. The ideal Taylor dispersion experiment.

completely, it is of uniform composition over this cross section, and is supposed to extend infinitesimally in the axial direction. The only perturbation of the flowing stream therefore arises from the change in the concentration of component 1 at $z = 0$, which may be represented by a delta-function, $\delta(z)$, which is normalized so that

$$\pi a_0^2 \int_{-\infty}^{\infty} \delta(z) [C_{1i} - C_{1f}] dz = N_1 \quad (1)$$

where $\delta(z) = 0$ for $z \neq 0$, and N_1 represents the number of moles of component 1 in the sample in excess of those present in the same volume of the flowing stream.

The concentration gradient established by the introduction of this sample, together with the action of the parabolic velocity profile of laminar flow, results in dispersion of the pulse. The process of molecular diffusion involved is clearly that of mutual or interdiffusion and, in the present analysis, the appropriate diffusion coefficient, \mathcal{D}_{12} , is supposed to be independent of the composition of the liquid mixture.

If we denote the perturbation to the flowing stream composition caused by the pulse by $\Delta C_1(r, \theta, z, t)$, then the differential equation for ΔC_1 , describing the dispersion, is

$$\frac{1}{\mathcal{D}_{12}} \frac{\partial(\Delta C_1)}{\partial t} = \nabla^2(\Delta C_1) - \frac{2\bar{u}_0}{\mathcal{D}_{12}} \left[1 - 2 \left(\frac{r}{a_0} \right)^2 \right] \frac{\partial(\Delta C_1)}{\partial z} \quad (2)$$

and the conditions for its solution are, at $t = 0$,

$$\Delta C_1(r, \theta, 0, 0) = \delta(z)(C_{1i} - C_{1f}); \quad \delta(z) = 0 \text{ for } z \neq 0 \quad (3)$$

and

$$\frac{\partial(\Delta C_1)}{\partial r} = 0 \quad \text{at } r = a_0 \text{ for all } t \quad (4)$$

together with sufficient conditions on ΔC_1 for $z = \pm\infty$.

In his original analysis, Taylor [6] introduced an approximation concerning the relative magnitudes of axial and radial dispersion so as to render the solution of Eq. (2) practicable. However, here we prefer to follow the work of Aris [13], and to seek solutions for various spatial moments of the concentration distribution, since these turn out to be sufficient for the analysis of the experiment.

We define the p th spatial moment of the concentration distribution at a

radial position r about an origin moving with the mean velocity of the flow by the equation

$$c_p(r, \theta, t) = a_0^{p+1} \int_{-\infty}^{\infty} \xi^p \Delta C_1(\xi, r, \theta, t) d\xi \quad (5)$$

Here

$$\xi = (z - \bar{u}_0 t) / a_0 \quad (6)$$

denotes a dimensionless axial coordinate with respect to the moving origin. The moments of the distribution, averaged over a cross section of the tube, are then defined by the equation

$$m_p = \frac{1}{\pi a_0^2} \int_0^{2\pi} \int_0^{a_0} r c_p(r, \theta, t) dr d\theta \quad (7)$$

and the normalized moments by

$$\mu'_p = m_p / m_0 \quad (8)$$

Following the work of Aris [13], two sets of differential equations for c_p and m_p can then be derived from Eq. (1), which read

$$\begin{aligned} \frac{1}{\mathcal{D}_{12}} \frac{\partial c_p}{\partial t} &= \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c_p}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 c_p}{\partial \theta^2} + p(p-1) c_{p-2} \\ &+ \frac{\bar{u}_0}{\mathcal{D}_{12}} p \left(1 - 2 \left(\frac{r}{a_0} \right)^2 \right) c_{p-1} \end{aligned} \quad (9)$$

and

$$\begin{aligned} \frac{1}{\mathcal{D}_{12}} \frac{dm_p}{dt} &= p(p-1) m_{p-2} \\ &+ \frac{p\bar{u}_0}{a_0^2 \mathcal{D}_{12} \pi} \int_0^{2\pi} d\theta \int_0^{a_0} r \left(1 - 2 \left(\frac{r}{a_0} \right)^2 \right) c_{p-1} dr \end{aligned} \quad (10)$$

For the conditions of this analysis, sufficient conditions on the behavior of ΔC_1 at $\xi = \pm\infty$ are ensured by the fact that the sample introduced occupies a finite volume of the tube.

The solutions of Eqs. (9) and (10) for the present boundary conditions

have been given by Aris [13]. For the zeroth moment, averaged over a cross section, we obtain

$$m_0 = \text{constant} \quad \text{or} \quad \dot{\mu}_0 = 1 \quad (11)$$

which merely express conservation of mass. Furthermore,

$$m_1 = 0 = \dot{\mu}_1 \quad (12)$$

which expresses the fact that the mean of the distribution, averaged over a cross section, travels in the tube with the average velocity of the flow. The mean of the distribution as a function of radial position in the tube may be obtained as³

$$c_1 = -\frac{1}{4} \frac{\bar{u}_0 a_0^2}{\mathcal{D}_{12}} \left\{ \frac{1}{3} + \left(\frac{r}{a_0} \right)^2 - \frac{1}{2} \left(\frac{r}{a_0} \right)^4 \right\} + \frac{8\bar{u}_0 a_0^2}{\mathcal{D}_{12}} \sum_{n=1}^{\infty} \alpha_{0n}^{-4} \frac{J_0(\alpha_{0n} r/a_0)}{J_0(\alpha_{0n})} \exp \left[-\alpha_{0n}^2 \mathcal{D}_{12} t/a_0^2 \right] \quad (13)$$

In this expression, α_{0n} represents the n th zero of $dJ_0(x)/dx$, where J_0 is the zeroth-order Bessel function of the first kind.

The cross-section averaged second moment, μ'_2 , may also be derived, and is given by the expression

$$u'_2 = 2 \left(\mathcal{D}_{12} + \frac{\bar{u}_0^2 a_0^2}{48 \mathcal{D}_{12}} \right) t - 128 \left(\frac{\bar{u}_0^2 a_0^4}{\mathcal{D}_{12}} \right) \sum_{n=1}^{\infty} \alpha_{0n}^{-8} [1 - \exp(-\alpha_{0n}^2 \mathcal{D}_{12} t/a_0^2)] \quad (14)$$

Aris was also able to show that the longitudinal distribution of concentration approaches that of a normal distribution as $t \rightarrow \infty$. The approach to normality occurs as t^{-1} , as can be seen, for example, from the expression for the skewness of the cross-section averaged distribution,

$$S = \mu_3'^2 / \mu_2'^3 \quad (15)$$

which is given asymptotically by the relation [13]

³The authors are grateful to W. Baldauf for drawing their attention to an error in the original expression given by Aris [13].

$$S = \frac{49 \bar{u}_0^6 a_0^8}{2^{20} \mathcal{D}_{12}^7 \left[1 + \frac{\bar{u}_0^2 a_0^2}{48 \mathcal{D}_{12}^2} \right]^3 t} \quad (16)$$

Equations (12) and (14) yield the fundamental working equations for the analysis of the ideal experiment. We first note that the exponential transient term in Eq. (14) can be made to decay arbitrarily rapidly by the choice of suitable conditions. Thus for

$$\mathcal{D}_{12} t / a_0^2 > 0.6 \quad (17)$$

the transient terms contribute less than 0.01% to the second term of Eq. (14). Hence provided that Eq. (17) is satisfied, Eq. (14) may be written

$$u'_2 = 2 \left(\mathcal{D}_{12} + \frac{\bar{u}_0^2 a_0^2}{48 \mathcal{D}_{12}} \right) t - \frac{128 \bar{u}_0^2 a_0^4}{\mathcal{D}_{12}^2} \left\{ \frac{1}{(3.8317)^8} + \frac{1}{(7.0156)^8} + \dots \right\}$$

Because the mean velocity of the flow can be chosen independently of the time t , we note that if

$$\bar{u}_0 > 700 \mathcal{D}_{12} / a_0 \quad (19)$$

then Eq. (18) can be reduced to the form

$$\mu'_2 = \frac{\bar{u}_0^2 a_0^2}{24 \mathcal{D}_{12}} t - \frac{128 K \bar{u}_0^2 a_0^4}{\mathcal{D}_{12}^2} \quad (20)$$

with an associated error of less than 0.01%, which we regard as negligible. In this equation, we have written

$$K = \sum_{n=2}^{\infty} \alpha_{0n}^{-8} = 2.1701 \dots \times 10^{-5} \quad (21)$$

for convenience. It can be shown that, for measurements in liquids, condition (19) is easily satisfied while maintaining the fluid flow in the laminar regime.

Equation (20) could evidently form the fundamental working equation for the ideal experiment, since the diffusion coefficient \mathcal{D}_{12} could be derived from experimental measurements of the second moment, μ'_2 , with the aid of it. However, for later use it is more convenient to employ a limiting form of this equation. Since the duration, t , of the measurement may be chosen arbitrarily

ly, we note that the time independent term in Eq. (20) may be made negligible (<0.01%) by choosing

$$\mathcal{D}_{12}t/a_0^2 > 700 \quad (22)$$

This selection automatically ensures that the transient term in Eq. (14) is even smaller than that corresponding to condition (17). In this case, Eq. (20) reduces to the very simple form

$$\mu'_2 = \frac{\bar{u}_0^2 a_0^2}{24 \mathcal{D}_{12}} t = \mu'_{20} \quad (23)$$

where the subscript (0) implies the satisfaction of conditions (19) and (22) in the experiment. Furthermore, by virtue of Eq. (12), the mean velocity of the fluid \bar{u}_0 may be determined from the first moment of the distribution with respect to the fixed origin $z = 0$. Denoting the first moment by \bar{z} , it follows that

$$\bar{u}_0 = \bar{z}/t \quad (24)$$

so that the final working equation for the ideal diffusion experiment becomes

$$\mathcal{D}_{12} = \frac{\bar{z}^2 a_0^2}{24 \mu'_{20} t} \quad (25)$$

A diffusion coefficient determination may therefore be performed by measurement of just the first and second spatial moments of the cross-section averaged concentration distribution after flow for a time t in a tube of known radius.

If condition (22) is not satisfied, the second moment required in Eq. (25) can still be derived from the measured moment, μ'_2 , by application of the correction $\delta\mu'_{21}$ in the form

$$\mu'_{20} = \mu'_2 + \delta\mu'_{21} \quad (26)$$

where

$$\delta\mu'_{21} = \frac{128 K \bar{u}_0^2 a_0^4}{\mathcal{D}_{12}^2} \quad (27)$$

Provided that

$$\mathcal{D}_{12}t/a_0^2 > 10 \quad (28)$$

the correction $\delta\mu'_{21}$ amounts to no more than 0.6% of μ'_{21} , and so may be calculated with sufficient accuracy using an estimate for \mathcal{D}_{12} .

Finally, in this section we record for future use that if conditions (19) and (20) are satisfied, then the absolute skewness of the spatial distribution is less than 5×10^{-8} , so that for practical purposes the distribution may be regarded as normal. Furthermore, it follows that the Taylor dispersion process under the conditions specified may be equally well described by the one-dimensional differential equation for the concentration perturbation averaged over a cross section, ΔC_{1m} . This equation reads [6, 13]:

$$E \frac{\partial^2(\Delta C_{1m})}{\partial z^2} - \bar{u}_0 \frac{\partial(\Delta C_{1m})}{\partial z} = \frac{\partial(\Delta C_{1m})}{\partial t} \quad (29)$$

where E is an effective diffusivity

$$E = \frac{a_0^2 \bar{u}_0^2}{48 \mathcal{D}_{12}} \quad (30)$$

This one-dimensional representation is equivalent to the process of plug flow plus axial diffusion with a diffusivity E , and the moments of its solution are identical to those for the solution of the full diffusion equation for the conditions detailed above.

3. PRACTICAL CONSIDERATIONS

The ideal experimental method outlined in the previous section is not practicable for measurements of diffusion coefficients. Furthermore, even if it were, it would not be possible to construct an apparatus to exactly conform with the ideal. In order to perform such measurements using the same principle it is therefore necessary to make changes to the experimental method and to examine the ways in which a practical instrument differs from the ideal. In the following sections of this paper we examine the consequences of these considerations for the design of an instrument and the working equations for the analysis of experimental data. In this examination, we shall presume that all departures from the ideal model are small, so that they may all be treated as first-order perturbations. In this case, we may further suppose that the interaction between any two or more of these first-order effects is negligible and that therefore we may treat each perturbation independently. The conditions under which such assumptions are valid will, of course, emerge from the analysis and form the basis of design criteria.

The departures of a practical instrument from the ideal may be classified under four headings:

1. Concentration distribution determination
2. Sample introduction
3. Diffusion tube geometry
4. Concentration dependent fluid properties

In the following sections, we examine each of these in turn, and, where it is appropriate, express the effect of the departure from the ideal instrument as a small correction to the ideal working equations. In some cases, it will be possible to render the corrections negligible by proper design. In other cases, the correction can only be made small by design, but then it can be estimated with sufficient accuracy to make the contribution to the overall uncertainty in the diffusion coefficient measurements negligible.

4. CONCENTRATION DISTRIBUTION DETERMINATION

4.1. Temporal Moments

We first consider the fact that it is experimentally much more convenient to observe the concentration distribution at a particular cross section in the tube as a function of time, rather than to observe it at one instant of time as a function of axial position. We therefore consider again the diffusion process described earlier in the ideal apparatus, but now we suppose that we can determine the cross-section averaged perturbation of the concentration of component 1, denoted by ΔC_{1m} , at an axial position $z = L$, in an infinitesimally small length of the diffusion tube. Then, in order to relate the temporal moments of the distribution observed in this way to the spatial moments of the previous section, we use the result derived there that the spatial distribution is essentially normal.

Thus we write [6] for ΔC_{1m} ,

$$\Delta C_{1m} = \frac{N_1}{\sqrt{2} \pi^{3/2} a_0^2 \mu_2'^{1/2}} \exp \left\{ -\frac{(z - \bar{u}_0 t)^2}{2\mu_2'} \right\} \quad (31)$$

For an observation carried out in the cross section at the axial position $z = L$, we define

$$\tau = \bar{u}_0 t / L$$

and

$$\zeta = \mu_2' / 2\bar{u}_0 L t$$

We can then rewrite Eq. (31) in the form

$$\Delta C_{1m} = \frac{N_1}{2\pi a_0^2 L} (\pi \zeta \tau)^{-1/2} \exp \left\{ \frac{-(1-\tau)^2}{4\zeta \tau} \right\} \quad (32)$$

The normalized, temporal moments of this distribution, for a measurement carried out in the idealized apparatus, $[\mu_p]_{id}$, are then defined by the equation

$$[\mu_p]_{id} = \left(\frac{L}{\bar{u}_0} \right)^p \int_0^\infty \tau^p \Delta C_{1m} d\tau \Bigg/ \int_0^\infty \Delta C_{1m} d\tau \quad (33)$$

In general, the quantity ζ is time dependent, as a result of the definition of μ'_2 in Eq. (20), and the analytic evaluation of Eq. (33) is impossible. Consequently, we seek approximate solutions for the temporal moments. Because the time dependent part of ζ is generally small [$<0.6\%$ if condition (28) is satisfied], these approximations will prove sufficiently accurate.

4.1.1. Zeroth-Order Approximation

If both conditions (19) and (22) are satisfied, then, with negligible error,

$$\zeta = \zeta_0 = \mu'_{20}/2\bar{u}_0 L t = \bar{u}_0 a_0^2 / 48 L \mathcal{D}_{12} \quad (34)$$

which is time independent, and evaluation of the first temporal moment $[\mu_1]_{id} \equiv \bar{t}_{id}$ leads to result of Pratt and Wakeham [14],

$$\bar{t}_{id} = \frac{L}{\bar{u}_0} (1 + 2\zeta_0) \quad (35)$$

Under the same conditions, the second raw temporal moment, derived by Levenspiel and Smith [15] is

$$[\mu_2]_{id} = \left(\frac{L}{\bar{u}_0} \right)^2 \left\{ 1 + 6\zeta_0 + 12\zeta_0^2 \right\}$$

so that the temporal variance of the distribution, denoted by σ_{id}^2 , may be written

$$\sigma_{id}^2 = \left(\frac{L}{\bar{u}_0} \right)^2 \{ 8\zeta_0^2 + 2\zeta_0 \} \quad (36a)$$

$$= \frac{8\zeta_0^2 + 2\zeta_0}{(1 + 2\zeta_0)^2} (\bar{t}_{id})^2 \quad (36b)$$

Here we have used the subscript (id) to denote that the various moments refer to measurements in the ideal diffusion apparatus of the previous section. Equation (36) can be solved exactly for ζ_0 to yield

$$\zeta_0 = \frac{2\sigma_{id}^2 - \bar{t}_{id}^2 + \{\bar{t}_{id}^4 + 4\bar{t}_{id}^2\sigma_{id}^2\}^{1/2}}{\{8\bar{t}_{id}^2 - 4\sigma_{id}^2\}} \quad (37)$$

Finally, from Eqs. (35) and (23), we note that

$$\mathcal{D}_{12} = \frac{(1 + 2\zeta_0)}{\zeta_0} \frac{a_0^2}{48\bar{t}_{id}} \quad (38)$$

so that using Eq. (37) in (38), we obtain the final working equation for the experiment in the form

$$\mathcal{D}_{12} = \frac{a_0^2}{24\bar{t}_{id}} \left\{ \frac{[1 + 4\sigma_{id}^2/\bar{t}_{id}^2]^{1/2} + 3}{\{([1 + 4\sigma_{id}^2/\bar{t}_{id}^2]^{1/2} + 2\sigma_{id}^2/\bar{t}_{id}^2 - 1)\}} \right\} \quad (39)$$

With this equation the diffusion coefficient can be determined from measurements of the first two temporal moments of the concentration distribution at a particular cross section of the diffusion tube.

4.1.2. First-Order Approximation

If condition (19) is satisfied, but the measurement time, t , is such that condition (22) is not satisfied, it is still possible to obtain an analytic working equation provided that the somewhat weaker condition (28) on the diffusion time is met. In this case, we write

$$\zeta = \zeta_1 = \zeta_0 + \delta\zeta$$

where

$$\delta\zeta = \frac{64K\bar{u}_0 a_0^4}{L\mathcal{D}_{12}^2 t}$$

We note now that the major contribution to the integrals in Eq. (33) arises from near $\tau = 1$, so that we may employ a quasisteady-state approximation to evaluate the small correction $\delta\zeta$. That is, we evaluate $\delta\zeta$ at $t = L/\bar{u}_0$, so that

$$\delta\zeta = - \frac{64K a_0^4 \bar{u}_0^2}{L^2 \mathcal{D}_{12}^2}$$

and thus ζ_1 can, within this approximation, be treated as time independent. We may now carry through the procedures of the zeroth-order analysis again, using ζ_1 in place of ζ_0 , and we find for the final working equation

$$\mathcal{D}_{12} = \frac{a_0^2}{24\bar{t}_{id}} \left\{ \frac{[1 + 4\sigma_{id}^2/\bar{t}_{id}^2]^{1/2} + 3}{[1 + 4\sigma_{id}^2/\bar{t}_{id}^2]^{1/2} + 2\sigma_{id}^2/\bar{t}_{id}^2 - 1} \right\} \times \left\{ \frac{1}{2} + \frac{1}{2}(1 - \delta_a)^{1/2} \right\} \quad (40)$$

where

$$\delta_a = (768)^2 K \zeta_0$$

and ζ_0 is defined by Eq. (37). Again, the working equation relates the diffusion coefficients to the first two temporal moments of the distribution observed in the ideal diffusion tube. Provided that condition (28) is satisfied, the term δ_a contributes at most 0.6% to the measured diffusion coefficient, so that the foregoing analysis for its estimation is sufficiently accurate.

In summary then, Eqs. (39) and (40) constitute the fundamental working equations for the evaluation of diffusion coefficients from temporal moment measurements in an ideal diffusion apparatus subject to the conditions

$$\mathcal{D}_{12}t/a_0^2 > 10 \quad \text{and} \quad \frac{\bar{u}_0 a_0}{\mathcal{D}_{12}} > 700$$

We note also that if $\mathcal{D}_{12}t/a_0^2 > 10$, then $\zeta_0 \leq 2 \times 10^{-3}$, so that Eqs. (36) and (38) may be linearized with respect to ζ_0 as was done earlier [14]. In this case, the approximate working equation, which we shall find useful later, becomes

$$\mathcal{D}_{12} = a_0^2 \bar{t}_{id} / 24\sigma_{id}^2 \quad (41)$$

with an error of no more than 1%.

4.2. The Concentration Monitor

The preceding analysis supposed that it was possible to determine the average concentration in a cross section of the diffusion tube at a particular axial position. In practice, such a measurement is not possible; rather, some average concentration in a finite length of the tube must be determined. There are two ways in which this may be accomplished and we consider them both here.

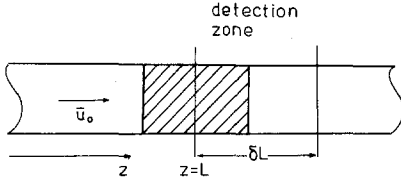


Fig. 2. The concentration monitor as a finite length of the diffusion tube.

4.2.1. A Section of the Diffusion Tube

In this concentration monitor, shown schematically in Fig. 2, we suppose that it is possible to determine the average perturbation to the concentration of the flowing stream in a small length δL of the diffusion tube itself beginning at $z = L$. We denote this average concentration perturbation by $\overline{\Delta C_1}$ and define it by the equation

$$\overline{\Delta C_1}(L, t) = \frac{1}{\pi a_0^2 \delta L} \int_L^{L+\delta L} \int_0^{a_0} \int_0^{2\pi} \Delta C_1(r, \theta, z, t) d\theta r dr dz \quad (42)$$

A composition monitor of this type could be employed when one of the components of the perturbing pulse is radioactive. In this case, the detector itself would consist of a test section of the diffusion tube within the field of view of a suitable activity monitor, which would define the length δL observed. This might be employed in measurements of self-diffusion coefficients of liquids. Clearly, owing to the finite volume of the detector the temporal moments of $\overline{\Delta C_1}$ will not be identical to those of ΔC_{1m} .

Introducing again the cross-section averaged composition perturbation ΔC_{1m} , we can write Eq. (42) in the form

$$\overline{\Delta C_1}(L, t) = \frac{1}{\delta L} \int_L^{L+\delta L} \Delta C_{1m} dz$$

If we suppose that all of our previous conditions are satisfied in the experiment, then we can use Eq. (31) for ΔC_{1m} , so that $\overline{\Delta C_1}(L, t)$ becomes

$$\Delta C_1 = \frac{N_1}{\sqrt{2} \pi^{3/2} a_0^2 \delta L (\mu'_{20})^{1/2}} \int_L^{L+\delta L} \exp \left[\frac{(z - \bar{u}_0 t)^2}{2\mu'_{20}} \right] dz \quad (43)$$

where for the present purposes, we have set $\mu_2 = \mu_{20}$. Evaluating the integral in Eq. (43), we obtain

$$\overline{\Delta C_1} = \frac{N_1}{2\pi a_0^2 \delta L} \left\{ \operatorname{erf} \left[\frac{(1 - \tau)}{(4\zeta_0^2 \tau)^{1/2}} + \frac{\delta L/L}{(4\zeta_0^2 \tau)^{1/2}} \right] - \operatorname{erf} \left[\frac{(1 - \tau)}{(4\zeta_0^2 \tau)^{1/2}} \right] \right\} \quad (44)$$

using the definitions of τ and ζ_0 given earlier.

In accordance with the approach outlined in Sec. 3, we now suppose that $\delta L/L$ is small; in particular, that

$$\delta L/L \ll (4\zeta_0\tau)^{1/2}$$

In this case we can expand the error function in Eq. (44) by a Taylor series and obtain

$$\begin{aligned} \overline{\Delta C_1}(L, t) = & \frac{N_1}{2\pi a_0^2 L} (\pi\zeta_0\tau)^{-1/2} \exp\left\{\frac{-(1-\tau)^2}{4\zeta_0\tau}\right\} \left\{1 - \frac{(1-\tau)}{(4\zeta_0\tau)} \left(\frac{\delta L}{L}\right) \right. \\ & \left. + \frac{1}{3(4\zeta_0\tau)} \left[\frac{2(1-\tau)^2}{(4\zeta_0\tau)} - 1\right] \left(\frac{\delta L}{L}\right)^2 + \dots\right\} \end{aligned} \quad (45)$$

This result allows computation of the normalized temporal moments of the distribution $\Delta C_1(L, t)$, defined in the standard manner. In particular, after some laborious algebra, we find for the first moment,

$$\bar{t} = \frac{L}{\bar{u}_0} \left(1 + 2\zeta_0 + \delta L/2L\right) \quad (46)$$

and for the variance

$$\sigma^2 = \left(\frac{L}{\bar{u}_0}\right)^2 \left[2\zeta_0 + 8\zeta_0^2 + \zeta_0(\delta L/L) + \frac{1}{12}(\delta L/L)^2\right] \quad (47)$$

correct to order $(\delta L/L)^2$.

Comparison of these equations with those for the moments of the ideal case, Eqs. (35) and (36), allows us to identify a correction to be applied to each measured moment to recover the ideal moments. Thus

$$\bar{t}_{\text{id}} = \bar{t} + \delta\bar{t}_1 \quad (48)$$

and

$$\sigma_{\text{id}}^2 = \sigma^2 + \delta\sigma_1^2 \quad (49)$$

Here

$$\delta\bar{t}_1 = -\delta L/2\bar{u}_0 \quad (50)$$

and

$$\delta\sigma_1^2 = -\delta L \left\{ \frac{a_0^2}{48\mathcal{D}_{12}\bar{u}_0} + \frac{\delta L}{12\bar{u}_0^2} \right\} \quad (51)$$

so that both corrections may be calculated from a knowledge of the mean flow velocity and an estimate of the diffusion coefficient. For the purpose of design, we may assume $\bar{u}_0 = L/\bar{t}_{id}$, and that $\mathcal{D}_{12}t/a_0^2 \geq 10$. With these approximations we find

$$\delta\bar{t}_1/\bar{t}_{id} \leq \frac{\delta L}{2L}$$

and

$$\delta\sigma_1^2/\sigma_{id}^2 \leq \frac{\delta L}{L} \left\{ \frac{1}{2} + 20 \frac{\delta L}{L} \right\}$$

so that if $\delta L/L$ is chosen to be no more than 0.01, the corrections to neither moment amounts to more than 0.7%, and the method proposed for their estimation should be satisfactory.

4.2.2. A Small Volume at the Tube Exit

A second type of concentration monitor, and the one most commonly employed in the measurements reported so far, consists of a small sampling volume, V_D , placed at the exit of the diffusion tube. The concentration of the effluent from the tube in this volume is measured, usually with the aid of a refractive index detector [7, 8]. The differences between the moments observed with this type of detector and the ideal ones are difficult to analyze because the flow pattern and geometry of the sample volume are not well known. Consequently, we examine two extreme cases to set bounds on the effect and to provide guidance for the design of an instrument.

We first consider that within the sample volume the dispersion process proceeds unaltered and that the refractive index detector determines the average concentration of the dispersing material within it. In this case, the analysis is identical to that given above and, in terms of the detector volume, the corrections to the moments read

$$\delta\bar{t}_2 = -\frac{L}{\bar{u}_0} \left(\frac{V_D}{2\pi a_0^2 L} \right) \quad (52)$$

and

$$\delta\sigma_2^2 = -\left(\frac{L}{\bar{u}_0} \right)^2 \left\{ \zeta_0 \left(\frac{V_D}{\pi a_0^2 L} \right) + \frac{1}{12} \left(\frac{V_D}{\pi a_0^2 L} \right)^2 \right\} \quad (53)$$

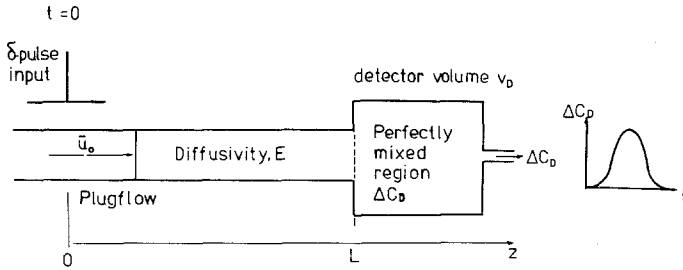


Fig. 3. The concentration monitor as a perfectly mixed volume, V_D , at the end of the diffusion tube.

An alternative model of the detector is that it acts as a perfectly mixed volume in which the composition is uniform. This model, which is probably slightly closer to reality, is illustrated schematically in Fig. 3. The presence of the perfectly mixed region implies that there now exists a boundary condition for the diffusion equation at the exit from the diffusion tube, and not at infinity, as described previously.

In order to analyze this problem, we first make use of the result given earlier, that to a very good approximation, the Taylor dispersion process for the conditions of interest here, $\mathcal{D}_{12}t/a_0^2 \geq 10$, may be described by means of the one-dimensional diffusion equation (29). For the model of the diffusion tube and detector shown in Fig. 3, the boundary conditions for the solution of this equation are: at $z = 0$,

$$\Delta C_{1m} = \delta(z)(C_{1i} - C_{1f})$$

and at $z = L$,

$$(54)$$

$$V_D \frac{\partial(\Delta C_D)}{\partial t} = -\pi a_0^2 E \left(\frac{\partial \Delta C_{1m}}{\partial z} \right)$$

where ΔC_D is the perturbation to the concentration in the detector volume. The second boundary condition implies that the concentration at the exit from the diffusion tube is identical with that in the entire detector volume.

The transfer function for this process has been given by Yano and Aratani [16] and reads

$$H(s) = \frac{2\beta \exp \{ (1/2\zeta_0)(1 - \beta) \}}{(2\alpha Ls/\bar{u}_0)(1 - \exp(-\beta/\zeta_0)) + (1 + \beta) - (1 - \beta) \exp(-\beta/\zeta_0)} \quad (55)$$

where

$$\beta = \left[1 + \frac{4\zeta_0 L s}{\bar{u}_0} \right]^{1/2}$$

and

$$\alpha = \frac{V_D}{\pi a_0^2 L}$$

is the ratio of the detector volume to the diffusion tube volume, and ζ_0 is defined by Eq. (34). In addition, s is the Laplace transform variable conjugate to the time t . The transfer function $H(s)$ can be used to derive the temporal moments of the concentration perturbation ΔC_D for a delta pulse input by means of the standard relation [17]

$$\mu_p = \lim_{s \rightarrow 0} (-1)^p \frac{dH(s)}{ds^p} \quad (56)$$

For the first moment, we find

$$\bar{t} = \left(\frac{L}{\bar{u}_0} \right) \left\{ 1 - \zeta_0 \left[1 - e^{-1/\zeta_0} \right] + \alpha (1 - e^{-1/\zeta_0}) \right\} \quad (57)$$

and for the variance,

$$\begin{aligned} \sigma^2 = & \left(\frac{L}{\bar{u}_0} \right)^2 \left\{ 2\zeta_0 (1 + 2e^{-1/\zeta_0}) + \zeta_0^2 (-5 + 4E^{-1/\zeta_0} + e^{-2/\zeta_0}) \right\} \\ & + \left(\frac{L}{\bar{u}_0} \right)^2 \left(\frac{V_D}{\pi a_0^2 L} \right)^2 \left\{ 1 - 2e^{-1/\zeta_0} + 2e^{-2/\zeta_0} \right\} \\ & + \left(\frac{V_D}{\pi a_0^2 L} \right) \left(\frac{L}{\bar{u}_0} \right) \left\{ 2\zeta_0 (1 - e^{-2/\zeta_0}) - 4e^{-1/\zeta_0} \right\} \end{aligned} \quad (58)$$

The choice of $\zeta_0 \leq 2 \times 10^{-3}$ for diffusion coefficient measurements implies that the exponential terms in Eqs. (57) and (58) are entirely negligible, and we obtain simply

$$\bar{t} = L/\bar{u}_0 \{ 1 - \zeta_0 + V_D/\pi a_0^2 L \}$$

and

$$\sigma^2 = (L/\bar{u}_0)^2 \left\{ (2\zeta_0 - 5\zeta_0^2) + \left(\frac{V_D}{\pi a_0^2 L} \right)^2 + 2\zeta_0 \left(\frac{V_D}{\pi a_0^2 L} \right) \right\}$$

The corrections to be applied to the moments observed with this detector in order to recover those of the ideal experiment can then be obtained by comparison with Eqs. (35) and (36a). That is,

$$\bar{l}_{id} = \bar{l} + \delta\bar{l}_3$$

and

$$\sigma_{id}^2 = \sigma^2 + \delta\sigma_3^2$$

where

$$\delta\bar{l}_3 = \frac{L}{\bar{u}_0} \left(3\zeta_0 - \frac{V_D}{\pi a_0^2 L} \right) \quad (59)$$

and

$$\Delta\sigma_3 = \left(\frac{L}{\bar{u}_0} \right)^2 \left\{ 13\zeta_0^2 - \left(\frac{V_D}{\pi a_0^2 L} \right)^2 - 2\zeta_0 \left(\frac{V_D}{\pi a_0^2 L} \right) \right\} \quad (60)$$

In both of these corrections, the first terms arise from the modifications of the diffusion process caused by the perfectly mixed region, whereas the remaining terms arise from the finite volume of the detector. These latter terms are naturally somewhat larger than those for an unmixed detector of the same volume given in Eqs. (52) and (53).

If, in a practical instrument, it is known which type of model detector most closely represents reality, then of course the appropriate correction terms given above should be employed. However, it is most likely that a practical detector will have a behavior intermediate between these two extremes. In this case, it is preferable to design the instrument so that the corrections evaluated for either model are negligible. For a fixed fluid velocity, and diffusivity, all the corrections can be made arbitrarily small by selection of the length of the diffusion tube, L , even if the detector volume, V_D , is dictated by external constraints.

4.3. Sample Introduction

Thus far we have been concerned with the evaluation of the temporal moments of the concentration distribution resulting from a δ -function injection of a sample at $z = 0$, which is uniform across the diffusion tube

cross section. In this section, we recognize that it is impossible to provide such a δ -function pulse in practice, but that it is relatively straightforward to introduce an approximately rectangular pulse of a sample into the tube at $z = 0$, which satisfies the condition that it be uniform across the diffusion tube. We therefore now consider the temporal moments of the concentration distribution detected in a cross section at $z = L$ as a result of an exactly rectangular input. For this input, the original boundary condition of Eq. (3) at $z = 0$ is modified to read

$$\begin{aligned}\Delta C_1(r, \theta, 0, t) &= (C_{1i} - C_{1f}) & 0 \leq t \leq t_i \\ \Delta C_1(r, \theta, 0, t) &= 0 & \text{otherwise}\end{aligned}\quad (61)$$

Here

$$t_i = \frac{V_i}{\pi a_0^2 \bar{u}_0}$$

and V_i is the volume of the sample injected. Rather than solve the complete Taylor dispersion problem subject to this new boundary condition, it is simpler to anticipate that the effect of the rectangular pulse is small and to use again the approximation that the dispersion process can be described by the one-dimensional diffusion equation (29). In this case, the problem is a standard one, and the results for the first moment and the variance observed at a fixed cross section in the tube are [16]

$$\begin{aligned}\bar{t} &= \frac{L}{\bar{u}_0} (1 + 2\zeta_0) + \frac{t_i}{2} \\ &= \frac{L}{\bar{u}_0} \left(1 + 2\zeta_0 + \frac{V_i}{2\pi a_0^2 L} \right)\end{aligned}\quad (62)$$

and

$$\begin{aligned}\sigma^2 &= \left(\frac{L}{\bar{u}_0} \right)^2 \left\{ 2\zeta_0 + 8\zeta_0^2 + \frac{t_i^2}{12} \right\} \\ &= \left(\frac{L}{\bar{u}_0} \right)^2 \left\{ 2\zeta_0 + 8\zeta_0^2 + \frac{1}{12} \left(\frac{V_i}{\pi a_0^2 L} \right)^2 \right\}\end{aligned}\quad (63)$$

The corrections required to correct moments observed using a square input pulse to the ideal ones for a δ -function pulse are therefore

$$\delta \bar{t}_4 = - \frac{L}{\bar{u}_0} \left(\frac{V_i}{2\pi a_0^2 L} \right) \quad (64)$$

and

$$\delta \sigma_4^2 = - \frac{1}{12} \left(\frac{L}{\bar{u}_0} \right)^2 \left(\frac{V_i}{\pi a_0^2 L} \right)^2 \quad (65)$$

As for the finite volume of the detector, the corrections are made smaller by increasing the diffusion tube volume for a fixed injection volume. Provided that the corrections can be made sufficiently small, departures from a true rectangular pulse will have an insignificant effect upon the observed moments. Since the volume of sample injected can be simply determined, both corrections are readily estimated.

5. DIFFUSION TUBE GEOMETRY

The analysis of the ideal experiment presumes that the diffusion tube is straight, and of uniform, circular cross section. The preceding two sections have established that in order to minimize corrections arising from the sample introduction and concentration distribution, the tube must be as long as possible for a fixed mean flow velocity. Since there is a practical lower limit to the flow velocity that can be held constant, this requirement normally requires a tube about 10 m long. Such a tube cannot be conveniently maintained at a constant temperature if it is straight, so it is usually wound in the form of a helix [14]. Furthermore, in order to satisfy condition (28), it is usual to employ tubes with an internal radius of about 0.5 mm, so that uniformity of the bore in manufacture is difficult to achieve. For the same reasons, exact circularity of the cross section cannot be assured. Finally, in order to couple together various items of equipment, it is sometimes necessary to use a small length of tubing of a different bore. In this section, we consider the implications of each of these effects for the first and second spatial moments of the concentration distribution in the tube, and hence diffusion coefficient measurements.

5.1. Helical Diffusion Tube

When the diffusion tube of internal radius a_0 is wound into a helical coil of radius R_c , the varying path lengths traversed by the fluid at different radial positions in the tube and the secondary flows present in the flow contribute to the dispersion process. This topic has been extensively studied, in view of its significance in physiological problems and in many engineering applications [18–21]. Consequently, it is sufficient for the present purpose to make use of these earlier studies.

Among the parameters that characterize the dispersion process in helical tubes, we consider the radius ratio

$$\omega = R_c/a_0 \quad (66)$$

the Reynolds number

$$\text{Re} = 2a_0\bar{u}_0\rho/\eta \quad (67)$$

the Schmidt number

$$\text{Sc} = \eta/\rho\mathcal{D}_{12} \quad (68)$$

and the Dean number

$$\text{De} = \text{Re}\omega^{-1/2} \quad (69)$$

The theoretical analysis of Erdogan and Chatwin [19] was based upon the assumption that the dispersion process could be described by a one-dimensional diffusion equation similar to Eq. (29), and that the velocity profile in the diffusion tube conformed to that given by Dean [22]. These conditions restricted the validity of their results to large values of ω and to cases where $\mathcal{D}_{12}t/a^2 \gg 1$. Nunge *et al.* [20], using a different approach, employed the velocity profile of Topakoglu [23], and were thereby able to extend the earlier analysis to small values of ω . Finally, Janssen [21] introduced the velocity profile of Dean and the condition $\mathcal{D}_{12}t/a^2 \gg 1$, but solved the resulting differential equation numerically for large values of ω . None of these analyses provides a description of the dispersion process in a closed form. Nevertheless, within the range of conditions of interest here, large ω , small values of the group De^2Sc , and $\mathcal{D}_{12}t/a^2 \gg 1$, the three treatments lead to essentially identical results. However, the approximate nature of the analyses implies that it is more prudent to employ the results to establish conditions under which the effects of tube curvature are negligible, rather than to attempt to use them to obtain corrections to spatial moments observed in a curved tube to correct them to those for a straight tube.

For this purpose, we employ the results of Nunge *et al.* [20] to examine the fractional difference between the spatial variance of the concentration distribution in a curved tube and that in a straight tube for the same average velocity. Because of the assumptions of the theoretical analysis, the first moments are necessarily identical. The second spatial moment difference may be written as

$$\Delta = \frac{[\mu'_2]_c - \mu'_{20}}{\mu'_{20}} = g(\text{Re}, \text{Sc}, \omega) \quad (70)$$

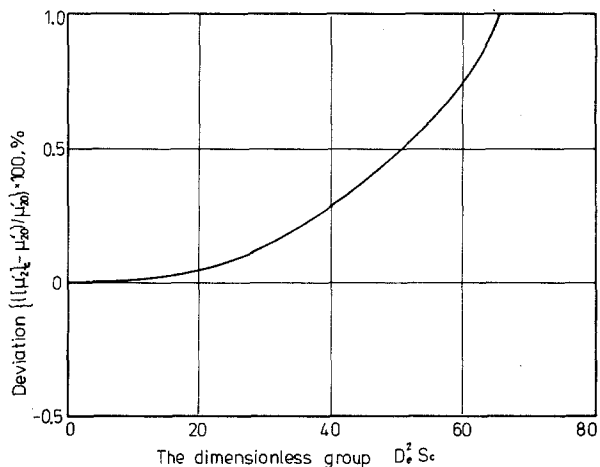


Fig. 4. The effects of tube coiling on the spatial variance of the concentration distribution for large coil radius to tube radius ratios, $\omega = R_c/a_0 \geq 100$.

where $[\mu'_2]_c$ is the second moment for the curved tube, and where, with sufficient accuracy for the present purpose [20],

$$\begin{aligned}
 g(Re, Sc, \omega) = & - \frac{192}{\omega^2} \left\{ \frac{4 Re^4}{576^2 \times 160} \left[\frac{-2569}{15,840} Sc^2 + \frac{109}{43,200} \right] \right. \\
 & + \frac{2 Re^2}{576 \times 144} \left[\frac{31}{60} Sc - \frac{25497}{13440} \right] \\
 & \left. + \left[\frac{419}{120 \times 196} + \frac{1}{4} \left(\frac{1}{Re^2 Sc^2} + \frac{1}{192} \right) \right] \right\} \quad (71)
 \end{aligned}$$

For the range of values of ω of interest here, $100 \leq \omega \leq 500$, the function $g(Re, Sc, \omega)$ is essentially dependent on the single dimensionless group De^2Sc as indicated by Janssen [21]. Consequently, in Fig. 4 we make use of this fact to provide a convenient representation of the behavior of $G(Re, Sc, \omega)$. The plot indicates that for any value of ω in the prescribed range, a choice of conditions such that

$$De^2Sc \leq 20$$

will ensure that coiling of the diffusion tube has an effect on the second central moment of the distribution no greater than $\pm 0.05\%$.

The above discussion provides a useful guide for the design of an instrument. Nevertheless, it should be emphasized that it will still be essential

to examine the effect of the diffusion tube curvature on the second moment experimentally for a particular instrument. This is easily accomplished, because the Dean number for the flow can be altered by using different flow velocities. Provided that the tube coiling effect is insignificant, it follows that the observed diffusion coefficients should be independent of the flow velocity within the precision of their measurement.

5.2. Nonuniform Diffusion Tube

A solution of the diffusion equation for steady flow in a straight tube of circular cross section, whose area varies in an arbitrary fashion along the axis of the tube, is not practical. Consequently, we consider a simple model of the possible nonuniformities in the cross-sectional area of the tube that has the benefit of relative simplicity and incorporates some of the features of the nonuniformities likely to be present in real tubes. Figure 5 contains a sketch of this model. The radius of the cross section of the tube is assumed to vary sinusoidally according to the equation

$$a(z) = a_0 \left(1 + \epsilon \sin \frac{2\pi z}{\lambda} \right) \quad (72)$$

We presume that the amplitude of the oscillations is small, $\epsilon \ll 1$, that the wavelength is large compared to the radius, $\lambda \gg a_0$, and that $\lambda \ll L$, the length of the tube.

In line with our earlier arguments, we seek to analyze the diffusion process in this nonuniform tube in an approximate manner so as to obtain the moments of the concentration distribution in the tube as a perturbation to those in a uniform tube with a constant radius a_0 for the same volumetric flow rate. Accordingly, we restrict the discussion to flows for which $\text{Re} |da/dz| \ll 1$, i.e., for which the lubrication approximation is valid. These flows are usually employed for the measurements in order to ensure laminar flow and satisfaction of condition (28). In this case, the Navier-Stokes equations reduce to the form [24]

$$\frac{\partial p}{\partial r} = \eta \left\{ \frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial}{\partial r} (r u_r) \right) + \frac{\partial^2 u_r}{\partial z^2} \right\}$$

$$\frac{\partial p}{\partial z} = \eta \left\{ \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial u_z}{\partial r} \right) + \frac{\partial^2 u_z}{\partial z^2} \right\}$$

and

$$\frac{\partial u_z}{\partial z} + \frac{1}{r} \frac{\partial}{\partial r} (r u_r) = 0$$

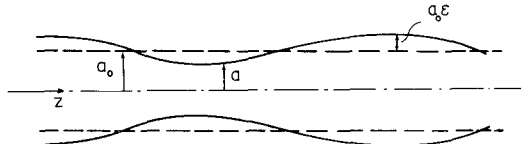


Fig. 5. The model of the nonuniform diffusion tube.

where use has been made of the cylindrical symmetry, and where u_z and u_r represent the axial and radial components of the fluid velocity, respectively. Furthermore, because $\partial^2 u_z / \partial z^2$ will be smaller than $\partial^2 u_z / \partial r^2$ by a factor of order $(a_0/\lambda)^2$, we may neglect the former term completely for the conditions specified above. In this case, we easily obtain the solutions for the two velocity components, correct to order $\epsilon a_0/\lambda$, as

$$u_z(r, z) = \frac{2Q}{\pi a^2} \left[1 - \left(\frac{r}{a} \right)^2 \right] \quad (73)$$

and

$$u_r(r, z) = \frac{4Q a_0 \epsilon}{\lambda a^2} \cos \left(\frac{2\pi z}{\lambda} \right) \left[\left(\frac{r}{a} \right) - \left(\frac{r}{a} \right)^3 \right] \quad (74)$$

where Q is the constant volumetric flow rate through the tube.

Anticipating, for simplicity, that the concentration distribution in the tube is cylindrically symmetric, as it was for the uniform tube, the diffusion equation may now be written as

$$\frac{1}{\mathcal{D}_{12}} \frac{\partial(\Delta C_1)}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \Delta C_1}{\partial r} \right) + \frac{\partial^2(\Delta C_1)}{\partial z^2} - u_z \frac{\partial \Delta C_1}{\partial z} - u_r \frac{\partial \Delta C_1}{\partial r} \quad (75)$$

The boundary conditions are, at $t = 0$,

$$\Delta C_1(r, 0, 0) = \delta(z)(C_{1i} - C_{1f})$$

and

$$\frac{\partial(\Delta C_1)}{\partial \nu} = 0 \quad \text{at } r = a(z) \text{ for all } t \quad (76)$$

where $\partial/\partial \nu$ indicates differentiation along the normal with respect to the tube wall.

We now write the velocity components and the concentration distribu-

tion for the nonuniform tube as perturbations to those for the uniform tube, so that

$$u_z(r, z) = u_0(r) + \epsilon u'_z \quad (77)$$

$$u_r(r, z) = \epsilon u'_r \quad (78)$$

and

$$\Delta C_1 = \Delta C_1^0 + \epsilon c' \quad (79)$$

where the superscript or subscript (0) denotes the concentration distribution in the uniform tube. Expansion of Eqs. (73) and (74) then shows that

$$u'_z = -4\bar{u}_0 \sin\left(\frac{2\pi z}{\lambda}\right) \left[1 - 2\left(\frac{r}{a_0}\right)^2\right] \quad (80)$$

and

$$u'_r = -\frac{4\bar{u}_0 a_0}{\lambda} \cos\left(\frac{2\pi z}{\lambda}\right) \left[\frac{r}{a_0} - \left(\frac{r}{a_0}\right)^3\right] \quad (81)$$

As we have noted earlier, for the conditions of interest, the contribution of axial molecular diffusion to the dispersion process is negligible. Consequently, following Taylor [6], we neglect the term $\partial^2(\Delta C_1)/\partial z^2$ in Eq. (74). Furthermore, making use of the fact that $\partial(\Delta C_1)/\partial z$, is, to a very good approximation [6, 14], independent of r , we see that the diffusion equation (74), to zeroth order in ϵ (i.e., for a uniform tube), is just that given by Taylor [6]. The temporal moments of the solution of this equation, averaged over a cross section, are therefore just the ideal moments given by Eqs. (35) and (36a).

To obtain the moments of the solution to first order in ϵ , we employ Eqs. (77)–(79) in the diffusion equation (75) and again neglect the longitudinal molecular diffusion term. Collecting terms of ϵ , we find the following equation for the concentration distribution perturbation c' in the nonuniform tube:

$$\frac{\partial c'}{\partial t} + u_0(r) \frac{\partial c'}{\partial z} + u'_z(r) \frac{\partial(\Delta C_1^0)}{\partial z} + u'_r \frac{\partial(\Delta C_1^0)}{\partial r} = \mathcal{D}_{12} \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c'}{\partial r} \right) \right] \quad (82)$$

To the same order in ϵ , the boundary condition of no molecular flux through the tube wall can be shown to be equivalent to

$$\frac{\partial(\Delta C_1)}{\partial r} = 0 \quad (83)$$

This is because the curvature of the wall, to first order, depends linearly on the product of ϵ with a_0/λ , and a_0/λ itself is presumed small, so that the curvature is essentially only a second-order effect.

We now use the fact that the term $u'_r \partial(\Delta C_1^0)/\partial r$ is very much smaller than $u'_z \partial(\Delta C_1^0)/\partial z$, because $\partial(\Delta C_1^0)/\partial r$ is small and because $u'_r/u'_z \sim O(a_0/\lambda)$. This justifies the neglect of the first of these terms in the diffusion equation (82) for the concentration distribution perturbation c' . Averaging Eq. (82) over a cross section of the tube, and making use of the boundary condition (83), we obtain

$$\frac{\partial c'_m}{\partial t} + \left(\overline{u'_z \frac{\partial(\Delta C_1^0)}{\partial z}} \right) + \overline{u_0(r) \frac{\partial c'}{\partial z}} = 0 \quad (84)$$

Here the subscript m denotes a concentration averaged over a cross section. In order to evaluate the remaining cross section averages, we again make use of the Taylor approximation [6] that $\partial(\Delta C_1^0)/\partial z$ is indistinguishable from $(\partial \Delta C_{1m}^0/\partial z)$, where ΔC_{1m}^0 is the cross-section averaged concentration in the uniform tube, and we also apply a similar approximation to $\partial c'/\partial z$. Thus we obtain the final differential equation as

$$\frac{\partial c'_m}{\partial t} + \overline{u'} \left(\frac{\partial \Delta C_{1m}^0}{\partial z} \right) + \overline{u_0} \left(\frac{\partial c'_m}{\partial z} \right) = 0 \quad (85)$$

Here, $\overline{u_0}$ is the mean velocity in the uniform tube, and $\overline{u'}(z)$ is the first-order perturbation to it in the nonuniform tube, given as

$$\overline{u'} = -2\overline{u_0} \sin \frac{2\pi z}{\lambda} \quad (86)$$

by averaging Eq. (73) over a cross section.

Now taking the Laplace transform of Eq. (85), we obtain

$$\frac{d\hat{c}'_m}{dz} + \left(\frac{\overline{u'}}{\overline{u_0}} \right) d \frac{\Delta C_{1m}^0}{dz} + \left(\frac{s}{\overline{u_0}} \right) \hat{c}'_m = 0 \quad (87)$$

Now it follows from Eq. (79) and the definition of the temporal moments of a distribution that to first order in ϵ , the raw moments in the nonuniform tube are related to those in the uniform tube by the expression

$$[\mu_p]_{\text{nu}} = [\mu_p]_{\text{id}} + \delta\mu_{p5} \quad (88)$$

where $\delta\mu_{p5}$ is proportional to ϵ and represents the perturbation to the ideal moments of the uniform tube. Using the results [17] that

$$\delta\mu_{p5} = \lim_{s \rightarrow 0} (-1)^p \frac{d^p c'_m}{ds^p}$$

and

$$[\mu_p]_{\text{id}} = \lim_{s \rightarrow 0} (-1)^p \frac{d^p (\Delta C_{1m}^0)}{ds^p}$$

we can employ Eq. (87) to construct differential equations for the perturbation to each moment. Differentiating Eq. (87) once with respect to s , reversing the order of differentiation, and taking the limit as $s \rightarrow 0$, we obtain for the first moment

$$\frac{1}{\epsilon} \frac{d(\delta\mu_{15})}{dz} + \frac{\bar{u}'}{u_0} \frac{d}{dz} (\bar{t}_{\text{id}}) = 0 \quad (89)$$

and after two differentiations of Eq. (87), we obtain in the limit $s \rightarrow 0$,

$$\frac{1}{\epsilon} \frac{d}{dz} (\delta\mu_{25}) + \frac{\bar{u}'}{u_0} \frac{d}{dz} [\mu_2]_{\text{id}} - \frac{2}{u_0 \epsilon} \delta\mu_{15} = 0 \quad (90)$$

Equation (89) is readily integrated using Eq. (86) for \bar{u}' and Eq. (35) for \bar{t}_{id} to yield the perturbation to the first moment observed at $z = L$ as

$$\delta\mu_{15} = \frac{\epsilon\lambda}{\pi u_0} \left[1 - \cos\left(\frac{2\pi L}{\lambda}\right) \right] \quad (91)$$

where we have made use of the fact that $\delta\mu_{15} = 0$ at $z = 0$, by virtue of the boundary conditions. Subsequently, Eq. (90) may be integrated using Eq. (35) for $[\mu_2]_{\text{id}}$ to yield at $z = L$

$$\delta\mu_{25} = \epsilon \left(\frac{2\lambda L}{\pi \bar{u}_0^2} + \frac{a_0^2 \lambda}{8\pi \mathcal{D}_{12} \bar{u}_0} \right) \left[1 - \cos\left(\frac{2\pi L}{\lambda}\right) \right] \quad (92)$$

The first moment observed in the nonuniform tube is therefore

$$[\mu_1]_{\text{nu}} = \frac{L}{\bar{u}_0} \left(1 + 2\zeta_0 \right) \left\{ 1 + \frac{\epsilon\lambda(1 - \cos(2\pi L/\lambda))}{\pi L(1 + 2\zeta_0)} \right\} \quad (93)$$

and this result, together with (88), (92), and the definition of the variance $[\sigma^2]_{\text{nu}} = [\mu_2]_{\text{nu}} - [\mu_1]_{\text{nu}}^2$, can be used to determine this central moment to first order in ϵ as

$$[\sigma^2]_{\text{nu}} = \left(\frac{L}{u_0}\right)^2 \left[8\zeta_0^2 + 2\zeta_0 \right] \left\{ 1 + \frac{\epsilon\lambda(1 - \cos(2\pi L/\lambda))}{\pi L(1 + 4\zeta_0)} \right\} \quad (94)$$

so that

$$\delta\sigma_5^2 = \frac{2L\lambda\zeta_0\epsilon}{\pi u_0^2} \left\{ 1 - \cos\left(\frac{2\pi L}{\lambda}\right) \right\} \quad (95)$$

From Eqs. (93) and (94), we first note that because, under practical conditions, $\zeta_0 \ll 1$, the correction to both moments is of order $\epsilon\lambda/L$. Because $\epsilon \ll 1$ and $\lambda/L \ll 1$ for the most likely practical situation, the corrections to both moments are small. For example, if the nonuniformity of the tube bore is of the order of 1% and $\lambda/L \sim 0.1$, then the correction to neither moment exceeds 0.06%. Moreover, as was shown earlier, to a very good approximation, the value of \mathcal{D}_{12} can be determined from Eq. (41), which for the nonuniform tube takes the form

$$\mathcal{D}_{12} = \frac{a_0^2 [\mu_1]_{\text{nu}}}{24 [\sigma^2]_{\text{nu}}} = \frac{a_0^2 \bar{t}_{\text{id}}}{24 \sigma_{\text{id}}^2} \quad (96)$$

by virtue of the smallness of ζ_0 . That is, to first order in ϵ , the effect of the nonuniformity of the diffusion tube bore upon the moments of the concentration distribution upon the evaluation of the diffusion coefficients only occurs in small terms ($\sim 1\%$) in the complete working equation of Eq. (40). Furthermore, these effects are themselves small, so that the overall contribution of nonuniformity to the evaluation of the diffusion coefficient from the observed moments is negligible, provided that the conditions of our analysis are met.

A final point of significance arising from the nonuniformity of the diffusion tube concerns the determination of the appropriate value of a_0 . It is easily shown that for the present model of the nonuniform tube, the volume of the tube to first order in ϵ is just

$$V_t = \pi a_0^2 L \left\{ 1 + \frac{\epsilon\lambda}{L\pi} \left[1 - \cos\left(\frac{2\pi L}{\lambda}\right) \right] \right\}$$

Thus if q^2 is determined from a measurement of the volume of the tube and

its length, the maximum error is of order $(\epsilon\lambda/L)$, which in practice can be made negligible by selection of tubing of a suitable quality.

5.3. Noncircular Cross Section

As in the case of the preceding section, we consider the effects of the noncircular cross section of the tube by means of a particular model. We suppose that the tube possesses an elliptical cross section with major and minor semiaxes a_1 and a_2 , respectively, so that the eccentricity e is given by

$$e = (1 - a_2^2/a_1^2)^{1/2}$$

Aris [13] has examined the problem of Taylor dispersion in such a tube, and from his work it may be shown that in such a situation the simplified working equation (41) for circular tubes must be replaced by the equation

$$\mathcal{D}_{12} = \frac{f(e)a_1^2\bar{t}}{24\sigma^2} \quad (97)$$

where μ and σ^2 are the first raw temporal moment and variance observed in the elliptical tube, and

$$f(e) = \frac{24 - 24e^2 + 5e^4}{24 - 12e^2} \quad (98)$$

In practice, it is not convenient to determine the ellipticity of a tube, or either semiaxis directly. However, by means of the measurement of the volume of the tube and its length, it is possible to determine the cross-sectional area of the tube, A , where

$$A = \pi a_1 a_2 = \pi a_1^2 (1 - E^2)^{1/2}$$

Therefore, consider the result of evaluating the diffusion coefficient from experimentally determined moments \bar{t} and σ^2 in an elliptical tube by means of the equation

$$\mathcal{D}'_{12} = \frac{A \mu_1}{24\pi \sigma^2} \quad (99)$$

Here the prime indicates that the diffusion coefficient calculated in this way differs from that evaluated according to Eq. (97). The ratio of the diffusion

coefficient calculated in this way to true value, \mathcal{D}_{12} , is

$$\frac{\mathcal{D}'_{12}}{\mathcal{D}_{12}} = \frac{A}{\pi a_1^2 f(e)} = \frac{(1 - e^2)^{1/2}}{f(e)} \quad (100)$$

Expanding the ratio in powers of the eccentricity, e , we find that

$$\frac{\mathcal{D}'_{12}}{\mathcal{D}_{12}} = 1 - \frac{14}{24} e^4 + \dots$$

which indicates that for small eccentricities, to equate \mathcal{D}_{12} to \mathcal{D}'_{12} would be a very good approximation. Indeed, direct numerical evaluation of the ratio $\mathcal{D}_{12}/\mathcal{D}'_{12}$ through Eq. (100) shows that even when $e = 0.5$ ($a_2/a_1 = 0.866$), the ratio amounts to 1.007, whereas when $e = 0.2$ ($a_2/a_1 = 0.98$), it departs by only 0.01% from unity. We see therefore that Eq. (99) may be used for the interpretation of experimental data even if the diffusion tube has an elliptical cross section, provided that the cross-sectional area of the tube is determined experimentally. As long as the eccentricity of the tube is not greater than 0.2, the experimental data may be evaluated using Eq. (40), with negligible error, inserting A/π in place of a_0^2 .

5.4. Connecting Tube

In order to consider the effect of adding to the exit of the diffusion tube a short length of connecting tubing of a different diameter, we again employ an approximate treatment. As before, this is justified by the small magnitude of the effect to be considered. We suppose the connecting tube, radius a_c , to be joined to the diffusion tube as shown in Fig. 6 so that the junction occurs at $z' = 0$. We assume that there is a sharp transition in the flow pattern in the tube from the fully developed profile of laminar flow in the diffusion tube to that fully developed profile characteristic of the connecting tube. If \bar{u}_c denotes

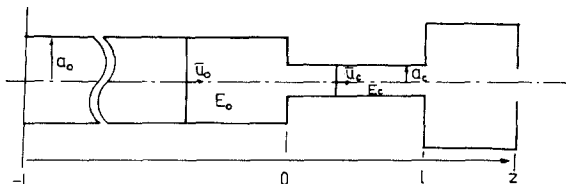


Fig. 6. The connecting tube between the diffusion tube and the detector.

the mean flow velocity in the connecting tube, then clearly, by virtue of continuity,

$$a_0^2 \bar{u}_0 = a_c^2 \bar{u}_c$$

We further suppose that the diffusion tube and the connecting tube extend to infinity in either direction about $z' = 0$, and that the concentration distribution resulting mainly from dispersion in the diffusion tube is observed as a cross-section average at $z' = l$. It may be remarked that although detection would not actually be carried out in this way, the corrections to account for the use of other types of detector and the finite length of the tube have been given in Section 4.2.

In order to obtain the moments of the concentration distribution observed at $z' = l$, as a result of a sample injection into the diffusion tube, we use again the Taylor approximation that the diffusion process in each tube may be represented by a one-dimensional equation of the form of Eq. (29). This means that we ignore any transient effects in the entrance region to the connection tube. In particular, we employ the effective diffusion coefficient defined by the equation

$$E_c = \frac{a_c^2 \bar{u}_c^2}{48 \mathcal{D}_{12}}$$

which is analogous to that defined for the diffusion tube in Eq. (30). With these approximations, we first obtain the moments observed at $z' = l$ in response to a δ -pulse injected at $z' = 0$, and in this calculation we allow dispersion both upstream and downstream of $z' = 0$. Fortunately, we do not need to carry out a detailed analysis here, since a very similar problem has already been solved by van der Laan [25]. His treatment is easily adapted to the present case, and yields, for the first raw moment \bar{t}_c and the variance σ_c^2 ,

$$\bar{t}_c = \frac{l}{\bar{u}_c} \left(1 + \zeta_c \left(1 + \frac{a_c^2}{a_0^2} \right) \right) \quad (101)$$

and

$$\sigma_c^2 = \left(\frac{l}{\bar{u}_c} \right)^2 \left\{ 2\zeta_c + \zeta_c^2 \frac{a_c^2}{a_0^2} \left(\frac{3a_c^2}{a_0^2} + 2 \right) \right\} \quad (102)$$

where

$$\zeta_c = \frac{a_c^2 \bar{u}_c}{48 \mathcal{D}_{12} l}$$

We now use the result that the first raw moment and second central moment of the response to any input function are just the moments of the response to a delta-pulse added to the appropriate moment of the input function. That is, we suppose that the input to the connecting tube is now provided by the concentration distribution resulting from Taylor dispersion in the diffusion tube, in the moments \bar{t}_{id} and σ_{id}^2 given by Eqs. (35) and (36a). In this case, the moments observed at $z' = l$ as a result of a delta-pulse injection at $z' = -L$ are

$$\mu_1 = \bar{t}_{id} + \bar{t}_c = \bar{t}_{id} + \delta \bar{t}_6 \quad (103)$$

and

$$\sigma^2 = \sigma_{id}^2 + \sigma_c^2 = \sigma_{id}^2 + \delta \sigma_6^2 \quad (104)$$

These equations enable us to identify corrections $\delta \bar{t}_6$ and $\delta \sigma_6^2$ to be added to the moments measured at $z' = l$ to recover the ideal moments. These corrections are given by the negative of the right-hand side of Eqs. (101) and (102), respectively, and may be easily estimated from a knowledge of the connecting tube geometry.

Using the results for the ideal moments, it may be shown that the fractional corrections to the observed moments are given approximately by the results

$$\delta \bar{t}_6 / \bar{t}_{id} = - \frac{a_c^2}{a_0^2} \left\{ \frac{l}{L} + \zeta_0 \left(1 + \frac{a_c^2}{a_0^2} \right) \right\}$$

and

$$\delta \sigma_6^2 / \sigma_{id}^2 = - \frac{a_c^4}{a_0^4} \left\{ \frac{l}{L} + \frac{1}{2} \frac{a_c^2}{a_0^2} \zeta_0 \left[3 \left(\frac{a_c}{a_0} \right)^2 + 2 \right] \right\}$$

Because ζ_0 itself is inversely proportional to L , the length of the diffusion tube, it may be seen that, as expected intuitively, reducing both the length and the radius of the connecting tube decreases the magnitude of the correction. For example, even if $l/L = 0.01$, the use of a connecting tube with a radius $a_c = a_0/4$ renders the correction to the first moment less than 0.1% and that to the variance less than $4 \times 10^{-3}\%$.

6. CONCENTRATION DEPENDENT FLUID PROPERTIES

In all of our analyses so far, it has been presumed that the properties of the fluid mixtures involved are independent of composition. In this section, we examine the consequences of the fact that both the diffusion coefficient to be measured and the density of the mixture depend on composition. Since the sample of the mixture injected is necessarily of a different composition from that of the flowing stream, the density of the mixture will vary from point to point in the diffusion tube, giving rise to the possibility of natural convective flows. Furthermore, the composition dependence of \mathcal{D}_{12} implies that we should examine again our solution of the diffusion equation for this case.

6.1. Concentration Dependent Diffusion Coefficient

Because it is not possible to solve the diffusion equation (2) for the case when \mathcal{D}_{12} is a function of C_1 , we consider instead an approximate treatment based upon that originally given by Taylor [6]. That is, we again recognize that to a very good approximation, under the conditions of interest, the dispersion process may be described by a one-dimensional diffusion equation describing the evolution of the cross-section averaged composition, which is characterized by the effective diffusion coefficient

$$E = \frac{a_0^2 \bar{u}_0^2}{48 \mathcal{D}_{12}(C_1)}$$

which is now supposed a function of C_1 . Following Taylor [6], we may then write the diffusion equation in the form

$$\frac{\partial(\Delta C'_{1m})}{\partial t} = \frac{\partial}{\partial \xi} \left(E \frac{\partial(\Delta C'_{1m})}{\partial \xi} \right) \quad (105)$$

where ξ is the axial distance with respect to the moving origin defined by Eq. (6). The initial condition for the solution is the injection of a δ -function pulse at $z = 0$ at time $t = 0$.

We now suppose that the composition variation of the molecular diffusion coefficient can, over a suitably small composition range, be represented by the equation

$$\mathcal{D}_{12}(\Delta C_{1m}) = \mathcal{D}_{12}^0 (1 - \chi \Delta C_{1m})$$

where \mathcal{D}_{12}^0 is the diffusion coefficient at the composition of the flowing stream. Thus we have

$$E(\Delta C_{1m}) = E^0 (1 + \chi \Delta C_{1m}) \quad (106)$$

where E^0 is the effective diffusivity at the composition of the flowing stream.

A perturbation solution of Eq. (105) with E given by Eq. (106) has been given by Hopkins [26]. The first-order perturbation solution may be written

$$\Delta C'_{1m}(x, t) = \Delta C^0_{1m} \left\{ 1 + \frac{N_1 \chi}{4\pi^{3/2} a_0^2 (E^0 t)^{1/2}} \left[\frac{\xi \sqrt{\pi}}{2(E^0 t)^{1/2}} \operatorname{erf} \left(\frac{\xi}{2(E^0 t)^{1/2}} \right) - \exp \left(-\xi^2 / 4E^0 t \right) \right] \right\} \quad (107)$$

Here, ΔC^0_{1m} is the solution when $E = E^0$ is a constant, which is, in the present notation,

$$\Delta C^0_{1m} = \frac{N_1}{2\pi^{3/2} (E^0 t)^{1/2} a_0^2} \exp \left(-\xi^2 / 4E^0 t \right)$$

Here, N_1 , defined by Eq. (1), again represents the number of moles of species 1 injected in the sample in excess of those present in the same volume of the flowing stream. The first and second spatial moments of this perturbed distribution can readily be evaluated with respect to the moving origin to lead to the result that

$$\mu''_1 = 0$$

and

$$\mu''_2 = 2E^0 t \left\{ 1 + \frac{N_1 \chi \left(\frac{5}{16} - \frac{1}{8\sqrt{\pi}} \right)}{\pi a_0^2 (2E^0 t)^{1/2}} \right\} \quad (108)$$

which we may write as

$$\mu''_2 = 2E(C_{1r})t$$

where

$$E(C_{1r}) = E^0 \left\{ 1 + \chi \frac{N_1 \left(\frac{5}{16} - \frac{1}{8\sqrt{\pi}} \right)}{\pi a_0^2 (2E^0 t)^{1/2}} \right\}$$

so that $E(C_{1r})$ is the value of E at a composition

$$C_{1r} = C_{1f} + \frac{N_1 \left(\frac{5}{16} - \frac{1}{8\sqrt{\pi}} \right)}{\pi a_0^2 (2E^0 t)^{1/2}} \quad (109)$$

Recalling the definition of E , we may then write

$$\mu_2'' = \frac{\bar{u}_0^2 a_0^2 t}{24 \mathcal{D}_{12}(C_{1r})}$$

which has exactly the same form as that of the working equation derived for the case of constant diffusivity. Hence we may conclude that if we employ Eq. (23) or its equivalent in terms of temporal moments [Eq. (40)], the diffusion coefficient obtained should be referred to the composition C_{1r} given by Eq. (109) and not to the composition of the flowing stream C_{1f} .

Because modern composition monitors, such as the refractive index detector, are very sensitive, the value of N_1 can usually be very small, and the reference concentration then departs insignificantly from that of the flowing stream.

6.2. Concentration Dependent Density

We must now consider the consequences of the fact that the liquid mixture sample injected into the flowing stream is necessarily of different density from that of the flowing stream. Because the concentration differences involved are small, we may write the density ρ at any point as a linear function of the concentration, so that

$$\rho = \rho_f(1 + \gamma \Delta C_1) \quad (110)$$

where ρ_f is the density of the flowing stream. The occurrence of density differences in the diffusion tube introduces two new effects into the dispersion process. First, the longitudinal density gradient leads to longitudinal pressure gradients that modify the velocity distribution in the flow. Second, the cross-sectional density gradients lead to a secondary flow driven by buoyancy forces. The equations of fluid mechanics governing this situation have not been analyzed exactly. However, Erdogan and Chatwin [19] have given an approximate treatment based upon the assumption that the density differences involved are small, and which is restricted to the region where the Taylor dispersion process has become one-dimensional. Under these conditions, they found that the evolution of the cross-section averaged concentration in the tube was controlled by the equation

$$\frac{\partial \Delta C_{1m}}{\partial t} = \frac{a_0^2 \bar{u}_0^2}{48 \mathcal{D}_{12}} \frac{\partial}{\partial \xi} \left\{ \frac{\partial \Delta C_{1m}}{\partial \xi} - \phi Q_2 \left(\frac{\partial \Delta C_{1m}}{\partial \xi} \right)^3 \right\} \quad (111)$$

Here Q_2 depends on the ratio $R = a_0 \bar{u}_0 / \mathcal{D}_{12}$ and the Schmidt number defined by Eq. (68):

$$Q_2 = -\left(\frac{1}{2880}\right)^2 \left[-\frac{2569}{8448} R^2 \text{Sc}^2 + \frac{19,797}{197,120} R^2 + \frac{10,425}{56} \text{Sc} + 60480 \frac{\text{Sc}^2}{R^2} \right]$$

The parameter ϕ is defined in terms of the coefficient γ by the equation

$$\phi = \left[\frac{\gamma g a_0^4 \rho^2}{\eta^2} \right]^2$$

where g is the acceleration due to gravity.

Further attention was also given to the problem by Barton [27, 28] and Smith [29]. They obtained approximate solutions of Eq. (111) and derived expressions for the spatial variance of the concentration distribution valid for the region in which the diffusion process is one-dimensional. For the case when N_1 extra moles of species 1 are introduced in the injection, Smith's result reads

$$\mu'_2 = \frac{a_0^2 \bar{u}_0^2}{24 \mathcal{D}_{12}} t + \sigma_{IT}^2 + \frac{12 \phi Q_2 \mathcal{D}_{12} N_1^2}{\pi^3 a_0^6 \bar{u}_0^2 3^{3/2} t} \quad (112)$$

In this equation σ_{IT}^2 represents the variance at the end of a transient period when the asymptotic solution becomes valid. Because this transient region has never been analyzed, Eq. (112), which is itself approximate, cannot form the basis of deriving a correction to the observed variance, which reduces it to the ideal moment in the absence of buoyancy. Neither can the equation provide a guidance as to the conditions under which buoyancy corrections are negligible. However, pending a more complete analysis of the problem, Eq. (112) does provide a means of deciding whether or not buoyancy effects are significant in particular measurements.

If Eq. (25), the working equation for the ideal experiment, is employed to determine the molecular diffusion coefficient from experimental measurements of the first and second spatial moments under conditions when buoyancy effects are significant, then Eq. (112) shows that the resulting apparent diffusion coefficients, \mathcal{D}_{12}^a , will differ from the true diffusion coefficient, \mathcal{D}_{12} . In fact,

$$\mathcal{D}_{12}^a = \mathcal{D}_{12} \left/ \left[1 + \frac{24 \sigma_{IT}^2 \mathcal{D}_{12}}{a_0^2 \bar{u}_0^2 t} + \frac{288 \epsilon Q_2 \mathcal{D}_{12}^2 N_1^2}{\pi^3 a_0^8 \bar{u}_0^2 3^{3/2} t^2} \right] \right. \quad (113)$$

Thus the apparent diffusion coefficient would depend upon the time of the measurement, t , the velocity of the flow \bar{u}_0 , as well as the magnitude of the initial concentration perturbation. Conversely, the absence of such dependen-

cies in experimental data implies that the results are not contaminated by buoyancy effects. It follows that at present, the only means to ensure that experimental measurements are free of the debilitating effects of buoyancy is to carry out measurements over a range of flow velocities and injection concentrations. Because buoyancy effects are minimized when the injection concentration is as near as possible to that of the flowing stream, measurements should be carried out with the smallest possible disturbance to this concentration.

7. SUMMARY

The foregoing analysis has shown that under the appropriate conditions, it is possible to design an instrument to measure liquid phase diffusion coefficients that departs in only small respects from the ideal description of it. Indeed, some of the departures from the ideal can be rendered so small as to be negligible. Other effects, although not negligible, may be made suitably small by the design so that corrections may be applied to account for them with some confidence. Here we summarize the results for the convenience of a designer and user of such an instrument.

Among the effects that can be rendered negligible are those which arise from the coiling of the diffusion tube and its nonuniformity. In order to eliminate coiling effects, conditions must be chosen so that

$$De^2Sc \leq 20$$

and that $\omega \geq 100$.

The nonuniformities of the diffusion tube bore are insignificant provided that the amplitude of the radius fluctuations, $a_0\epsilon$, and the length scale of their fluctuations are such that

$$\epsilon\lambda/L < 1 \times 10^{-3}$$

In view of both nonuniformities of the cross section and its possible noncircularity, the effective cross section tube should be determined from its volume and length. This measurement then renders effects due to any ellipticity in the cross section negligible provided that the ellipticity does not exceed $e = 0.2$. Buoyancy effects have not been accounted for exactly in the discussion, although a means for checking for their contribution to the dispersion experimentally has been proposed.

In addition, provided that conditions are chosen to satisfy the requirements of laminar flow,

$$\text{Re} = 2\bar{u}_0 a_0 \rho / \eta < 2000$$

and the additional constraints

$$\mathcal{D}_{12} t / a^2 \geq 10$$

and

$$a_0 \bar{u}_0 / \mathcal{D} > 700$$

the working equation for the analysis of the diffusion coefficient is

$$\mathcal{D}_{12} = \frac{A}{24\pi \bar{t}_{id}} \left\{ \frac{[1 + 4\sigma_{id}^2 / \bar{t}_{id}^2]^{1/2} + 3}{([1 + 4\sigma_{id}^2 / \bar{t}_{id}^2]^{1/2} + 2(\sigma_{id}^2 / \bar{t}_{id}^2) - 1)} \right\} \\ \times \left\{ \frac{1}{2} + \frac{1}{2} (1 - \delta_a)^{1/2} \right\}$$

where

$$\delta_a = (768)^2 K \zeta_0$$

and $K = 2.1701 \dots \times 10^{-5}$ while

$$\zeta_0 = \frac{2\sigma_{id}^2 - \bar{t}_{id}^2 + \{\bar{t}_{id}^4 + 4\bar{t}_{id}^2 \sigma_{id}^2\}^{1/2}}{\{8\bar{t}_{id}^2 - 4\sigma_{id}^2\}}$$

In these expressions, A is the cross-sectional area of the diffusion tube determined from its volume and length, and \bar{t}_{id} and σ_{id}^2 are the temporal first moment and variance in an ideal experiment. The latter quantities may be obtained from measurements of the same moments in a real experiment, \bar{t}_{expt} and σ_{expt}^2 , by application of the equations

$$\bar{t}_{id} = \bar{t}_{\text{expt}} + \sum_i \delta \bar{t}_i$$

and

$$\sigma_{id}^2 = \sigma_{\text{expt}}^2 + \sum_i \delta \sigma_i^2$$

where $\delta\bar{t}_i$ and $\delta\sigma_i^2$ are small corrections summarized below. In addition, the molar concentration of species 1 in the mixture to which the measured diffusion coefficient refers is C_{1r} , given by

$$C_{1r} = C_{1f} + \delta C_1$$

where δC_1 is a further small correction.

7.1. The Corrections

1. When the concentration monitor is part of the diffusion tube of length δL , the corrections are given by

$$\delta\bar{t}_1 = -\frac{L}{\bar{u}_0} \left(\frac{1}{2} \frac{\delta L}{L} \right)$$

$$\delta\sigma_1^2 = -\left(\frac{L}{\bar{u}_0} \right)^2 \left\{ \zeta_0 \left(\frac{\delta L}{L} \right) + \frac{1}{12} \left(\frac{\delta L}{L} \right)^2 \right\}$$

2. When the concentration monitor is a finite volume V_D at the end of the diffusion tube in which diffusion occurs unaltered, the corrections are given by

$$\delta\bar{t}_2 = -\frac{L}{\bar{u}_0} \left(\frac{V_D}{2\pi a_0^2 L} \right)$$

$$\delta\sigma_2^2 = -\left(\frac{L}{\bar{u}_0} \right)^2 \left\{ \zeta_0 \left(\frac{V_D}{\pi a_0^2 L} \right) + \frac{1}{12} \left(\frac{V_D}{\pi a_0^2 L} \right)^2 \right\}$$

3. When the concentration monitor is a perfectly mixed volume, V_D , at the end of the diffusion tube, the corrections are given by

$$\delta\bar{t}_3 = \left(\frac{L}{\bar{u}_0} \right) \left\{ 3\zeta_0 - \frac{V_D}{\pi a_0^2 L} \right\}$$

$$\delta\sigma_3^2 = \left(\frac{L}{\bar{u}_0} \right)^2 \left\{ 13\zeta_0^2 - \left(\frac{V_D}{\pi a_0^2 L} \right)^2 - 2\zeta_0 \left(\frac{V_D}{\pi a_0^2 L} \right) \right\}$$

4. For the finite injection volume V_i , the corrections are given by

$$\delta\bar{t}_4 = -\left(\frac{L}{\bar{u}_0} \right) \left(\frac{V_i}{2\pi a_0^2 L} \right)$$

$$\delta\sigma_4^2 = -\frac{1}{12} \left(\frac{L}{\bar{u}_0}\right)^2 \left(\frac{V_i}{\pi a_0^2 L}\right)^2$$

5. For a length of connecting tube between the diffusion tube and the detector volume, the corrections are given by

$$\delta\bar{t}_6 = \frac{l}{\bar{u}_0} \left(\frac{a_c}{a_0}\right)^2 \left\{ 1 + \frac{a_0^2}{a_c^2} \left(\frac{L}{l}\right) \zeta_0 \left(1 + \frac{a_c^2}{a_0^2} \right) \right\}$$

$$\delta\sigma_6^2 = \left(\frac{l}{\bar{u}_0}\right)^2 \left(\frac{a_c}{a_0}\right)^4 \left\{ 2 \frac{a_0^2}{a_c^2} \left(\frac{L}{l}\right) \zeta_0 + \frac{a_0^2}{a_c^2} \left(\frac{L}{l}\right)^2 \zeta_0^2 \left(\frac{3a_c^2}{a_0^2} + 2\right) \right\}$$

6. The correction to the reference composition is

$$\delta C_1 = \frac{N_1 \left(\frac{5}{16} - \frac{1}{8\sqrt{\pi}} \right)}{\pi a_0^2 (2\zeta_0 \bar{u}_0 L t)^{1/2}}$$

for an extra N_1 moles of species 1 injected.

It has been found that the sometimes conflicting conditions for a suitable design can all be satisfied in a practical instrument which will be described in a subsequent publication [30]. Furthermore, the residual corrections that need to be applied amount to no more than 0.5% in any case and are readily estimated. It is thus contended that the residual systematic errors in the application of the method of Taylor dispersion have been reduced to a level below that of the random errors of measurement.

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