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Turbulent flow in capillary gas chromatography — evaluation of a theoretical concept by Golay

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with appendix by

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ABSTRACT

Early in 1989, the late Marcel Golay derived a theory for turbulent flow capillary gas chromatography. He assumed that the flow pattern under turbulent conditions consists of a turbulent core separated from the tube wall by a very thin laminar flow layer. Further, it was assumed that the viscosity and the diffusion constant are uniform within the turbulent core. The core radius is a fraction ρ of the tube radius; the core viscosity is m times the laminar flow viscosity and the core diffusivity is assumed to be d times the laminar flow diffusion constant. Values for ρ , m and d have to be calculated from experimental data; ρ , m and d are essentially functions of Reynolds number (Re).

Using experimental data obtained in the laboratory, Golay's plate-height theory was evaluated for turbulent flow gas chromatography. In this verification an empirical relationship was used for the average turbulent diffusion constant as a function of Reynolds number and an empirical relationship for the thickness of the laminar sublayer. Further, it was assumed that $m = d$ (Reynolds' analogy). The experiments and theory agree fairly well at $Re = 6200$; at lower and higher values of Re the agreement is much poorer. The disagreement may be due to the empirical relationships used or to the postulations in the theory: Golay assumed a discontinuous change from laminar to turbulent viscosity and diffusion constants. In engineering literature often a gradual change in properties from the laminar sublayer to the turbulent and in the turbulent core is assumed.

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INTRODUCTION

An efficient way to increase the speed of analysis in capillary gas chromatography (GC) is to reduce the column diameter¹. However, minimization of the column diameter is limited by the drastic reduction in the working range. With present state-of-the-art detectors this point is reached at a column diameter of about 10 μm .

The foregoing approach lowers the contribution of the velocity profile (C_m term) to the chromatographic dispersion. In addition to a reduction in column diameter, this contribution can also be lowered by changing the velocity profile.

A possible way is to coil the column into a helix, which induces a secondary flow. This effect has been extensively described by Tijssen² and Tijssen *et al.*³ for GC and LC. Another way is to create turbulent flow. With turbulent flow the velocity profile is largely flattened, thus decreasing flow inequalities. Further, the effective diffusion coefficient is considerably increased by convective contributions. As a consequence, peak broadening arising in the mobile phase as a result of the velocity profile is expected to be substantially reduced. In a recent paper⁴, we described an instrumental set-up that permits the study of turbulent flow capillary GC. The experimental instrumentation included previously developed sample introduction, detection and recording systems compatible with peak widths in the millisecond range^{5,6}.

Existing theoretical models⁷⁻⁹ were evaluated experimentally. Only the Tijssen and Wittebrood theory⁹ gave acceptable agreement with the experimental plate heights at various capacity factors. For unretained components reduced plate heights, $h < 1$, were obtained at an average linear velocity of 15 m/s for column diameters of 320 μm . For a capacity factor $k = 1$ the reduced plate height increased by a factor of 15. Therefore, it was concluded that the gain in speed of analysis by turbulent GC is limited to solutes with low capacity factors.

During these experiments, we asked M.J.E. Golay, former Extraordinary Professor in our laboratory, for expert advice concerning the several contradictory theories on turbulent chromatography. He immediately became extremely interested in the subject. During the last months of his life he visited our laboratory several times and he derived a theory for turbulent dispersion in capillary GC. His manuscript "Calculations Relative to Turbulent Capillary Gas Chromatography" was meant to constitute his opening lecture at the 10th International Meeting on Capillary Chromatography in Riva del Garda, Italy, in May 1989. We were shocked by the message of his sudden death in his native country of Switzerland during the night of April 28-29, 1989. As a tribute to the great scientist Marcel Golay, inventor of capillary chromatography, we evaluate his postulates in this paper.

THEORY

In 1989, Golay derived a theory for turbulent dispersion in capillary GC¹⁰ in order to explain the experimental results to be presented in the following Experimental section. He extended the theory of Tijssen and Wittebrood⁹ towards general *sth* power velocity profile:

$$\frac{u}{\bar{u}} = \frac{s+2}{s} \left[1 - \left(\frac{r}{r_0} \right)^s \right] \quad (1)$$

where u is the velocity as a function of the radial coordinate and r_0 is the column radius.

This velocity profile has proved to be a good approximation for turbulent flow, where s changes from 5 to 10 for Reynolds numbers (Re) in the range $3000 < Re < 10^5$. For turbulent dispersion this finally leads to

$$C_m = \frac{r_0^2}{D_0} \cdot \frac{4 + (4s + 16)k + (s^2 + 10s + 20)k^2}{4(s + 4)(2s + 4)(1 + k)^2} \tag{2}$$

For a parabolic velocity profile ($s=2$), eqn. 2 reduces to the well known C_m term in the Golay–Giddings plate-height equation. For $s=10$, eqn. 2 gives the same result as that derived by Tijssen and Wittebrood⁹.

Later, Golay extended the theory in order to account for the laminar sublayer along the column wall. His original text, written in April 1989 (ref. 11), is given here in the Appendix.

The calculations are based on the assumption that the flow pattern under turbulent conditions consists of a turbulent core separated from the tube wall by a thin laminar flow layer (Fig. 1). It is also assumed that the diffusion constant and viscosity are uniform within the turbulent core. Data for the following variables have to be entered in the resulting equations:

- (1) the core radius r_t as a function of the tube radius r_0 :

$$r_t = \rho r_0 ; \rho < 1;$$

- (2) the core viscosity μ_t as a function of the known laminar flow viscosity μ_0 :

$$\mu_t = m\mu_0 ; m > 1;$$

- (3) the core diffusivity D_t as a function of the known laminar flow diffusion constant D_0 :

$$D_t = dD_0 ; d > 1.$$

Implied is also the postulate that ρ , m and d are essentially functions of the Reynolds

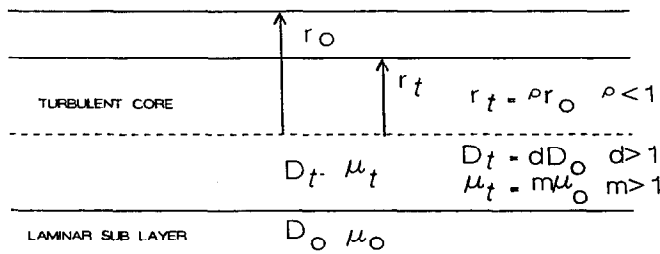


Fig. 1. Postulates made by Golay in his description of turbulent flow capillary GC.

number. Fortunately, Re is invariant within the tube as we pass from the high-pressure inlet side to the low-pressure outlet side.

If p_i and p_o are the inlet and outlet pressures, respectively, the gas velocity u in the laminar flow region at a distance r from the tube center ($r > r_t$) is given by

$$u = \frac{P_i^2 - P_o^2}{8p_o\mu_o L} (r_o^2 - r^2) \tag{3}$$

The velocity within the turbulent core is given by

$$u = \frac{p_i^2 - p_o^2}{8p_o L} \left(\frac{r_o^2 - r_t^2}{\mu_o} + \frac{r_t^2 - r^2}{\mu_t} \right) \tag{4}$$

The velocity profile is depicted schematically in Fig. 2.

Finally the plate height for turbulent dispersion can be written als follows¹¹:

The turbulent core:

$$H_1 = \frac{2dD_o\rho^2}{u_o} + \frac{u_o J r_o^2}{dD_o} \left(\frac{\alpha_1^2 \rho^4}{4} - \frac{\alpha_1 \rho^6}{3m} + \frac{\rho^8}{8m^2} \right) \tag{5}$$

where

$$J = \left[\frac{1}{1 - \left(1 - \frac{1}{m}\right)\rho^4} \right]^2$$

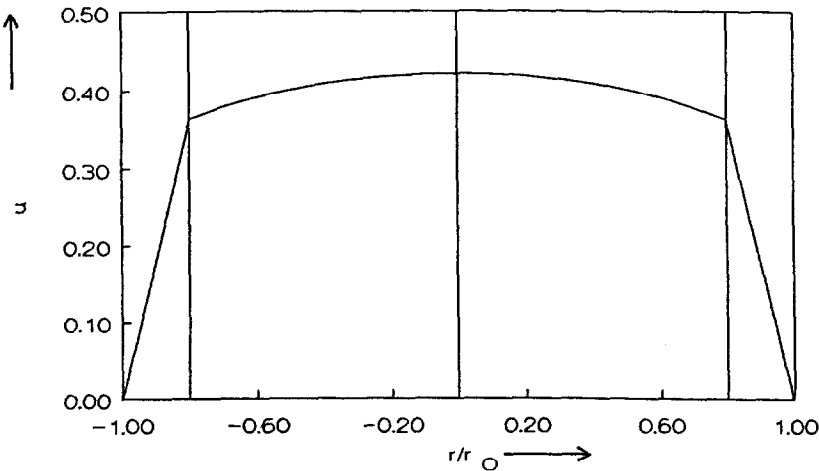


Fig. 2. Turbulent velocity profile. $m = d = 10$; $\rho = r_t/r_o = 0.8$.

and

$$\alpha_1 = \frac{1 + 2k - 2(1+k)\rho^2 + \rho^4}{(1+k)} + \frac{2(1+k)\rho^2 - \rho^4}{(1+k)m}$$

(2) The laminar region:

$$H_2 = \frac{2D_0(1-\rho^2)}{u_0} + \frac{u_0 J r_0^2}{4D_0} \left[\frac{\alpha_2^2(1-\rho^4)}{4} - \frac{\alpha_2(1-\rho^6)}{3} + \alpha_2\beta_2(1-\rho^2) + \frac{(1-\rho^8)}{8} - \frac{\beta_2(1-\rho^4)}{2} + \beta_2^2 \ln\left(\frac{1}{\rho}\right) \right] \quad (6)$$

where

$$\alpha_2 = \frac{1 + 2k + \rho^4}{1+k} - \frac{\rho^4}{(1+k)m}$$

$$\beta_2 = \rho^4 \left(\frac{1}{m} - 1 \right)$$

The total plate height $H = H_1 + H_2$.

The total plate height H can only be calculated if ρ , m and d are known. In this paper, empirical relationships will be used in order to verify Golay's theory.

According to the Reynolds' analogy, mass and momentum are transported by the same mechanism (under turbulent conditions) and, therefore, it is the authors' assumption that $m = d$. The turbulent diffusion coefficient can be written as

$$\frac{D_t}{D_0} = 1 + 0.009 Re^{0.84} Sc = d = m \quad (7)$$

where

D_t = average cross-sectional turbulent diffusion coefficient;

D_0 = molecular diffusion coefficient;

$Sc = \nu/D_0$ (ν = kinematic viscosity).

Using an empirical relationship for the thickness of the laminar sublayer¹², it follows that ρ can be written as

$$\rho = 1 - \left[\frac{68.4}{(0.5Re)^{0.875}} \right] \quad (8)$$

A computer program based on eqns. 5–8 was used to calculate the plate height as a function of the Reynolds number.

Under Results and Discussion, the results will be compared with experimentally determined plate heights.

EXPERIMENTAL

Experiments under turbulent flow conditions⁴ were performed with fused-silica columns of I.D. 320 μm , lengths ranging from 25 to 5 m and a stationary phase film thickness of 0.12 μm (CP SIL 5-CB; Chrompack, Middelburg, The Netherlands).

The sample introduction system consists of a pneumatically actuated Valco four-port valve (VICI AG; Valco, Schenkon, Switzerland) with an internal rotor (6 nl), which allows input band widths as low as 1 ms. The valve is mounted on top of a Carlo Erba (Milan, Italy) Model 4/60 gas chromatograph. The carrier gas (nitrogen) pressure was controlled with a Tescom (MN, U.S.A.) Model 44-1100 high-pressure regulator (up to 100 bar). A flame ionization detector could not be used as the flame was extinguished by the large carrier gas flow-rates. Therefore, a low-cell-volume (40 μl) photoionization detector (HNU Systems, Newton, MA, U.S.A.) was used throughout. The amplifier was modified to lower the time constant to about 2 ms.

Considering the high column flow-rates involved (> 1 l/min), peak broadening due to the cell volume will be extremely small. As ordinary chart-speed recorders are far too slow, chromatograms were recorded on a Model 3091 digital storage oscilloscope (Nicolet, Madison, WI, U.S.A.), capable of sampling at a maximum rate of 1 MHz.

RESULTS AND DISCUSSION

Using the theory of Golay (eqns. 5–8), which accounts for a laminar sublayer, the plate height could be calculated as a function of Re for various capacity factors. Under laminar conditions ($\rho = 1$, $m = 1$ and $d = 1$), it can be calculated that $H_1 = 0$ and H_2 is equal to the value predicted by the Golay–Giddings equation for laminar flow.

At $Re = 6200$ the results of the Golay theory accounting for a laminar sublayer are compared with the measured plate height as a function of k in Fig. 3. A very good fit is obtained. However, just as in the other theories⁹ and Golay using an n th power flow profile (eqn. 2), the fit becomes poorer at different Re numbers (see Table I). The reason is probably that in reality there is a gradual change of diffusion coefficient and viscosity from the laminar sublayer to the turbulent core. The theory assumes a discontinuous change from a molecular diffusion coefficient and viscosity to a turbulent diffusion coefficient and viscosity. More accurate diffusion and viscosity profiles have to be used. Another reason might be the empirical relationships used for ρ , m and d .

It should be noted that so far, the resistance to mass transfer in the stationary phase has been neglected. Considering the high carrier gas velocities involved (up to 15 m/s), the reliability of this assumption must be verified. The resistance to mass transfer in the stationary phase is not affected by the flow profile in the mobile phase^{8,13}. Assuming a liquid diffusion coefficient $D_1 \approx 10^{-5}$ cm^2/s (ref. 13), $k = 1$

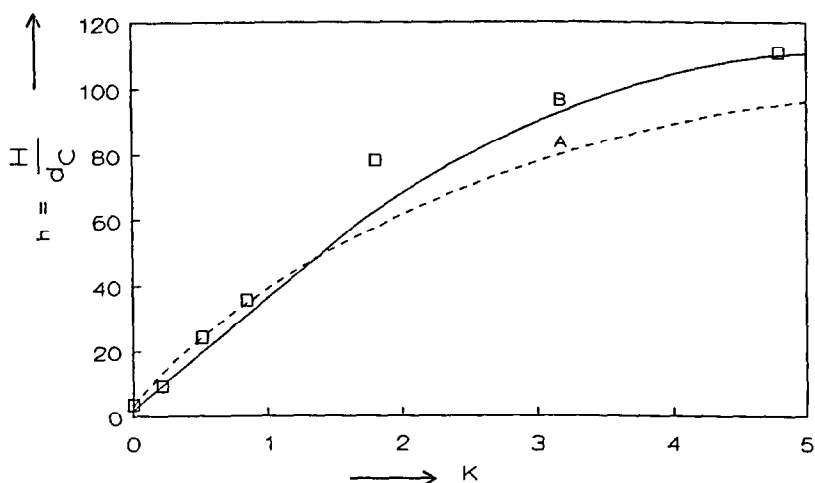


Fig. 3. Turbulent dispersion (reduced plate height, h) versus capacity factor ($Re = 6200$). \square = Experimental; A = measured according to the theory of Golay for an s th power flow profile; B = measured according to the theory of Golay accounting for a laminar sublayer.

TABLE I

REDUCED PLATE HEIGHTS, h

Re	Calculated h^{11}		Measured h	
	$k=0$	$k=1$	$k=0$	$k=1$
3000	1.2	42	7	63
6200	0.5	44	2.6	38
10 000	0.3	46	1	22

and $u = 15$ m/s ($Re = 10^4$), the reduced plate height of the resistance to mass transfer in the stationary phase is calculated to be $h_s = 0.22$. This may be considered negligible with respect to the foregoing results.

APPENDIX

Calculations relative to turbulent capillary gas chromatography^a

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^a This manuscript was compiled by Dr. Golay during the first week of April 1989, with the intention that, after some experiments and calculations, he would present it at the *10th International Symposium on Capillary Chromatography, May 22-25, 1989, in Riva del Garda*. His sudden death during the night of April 28-29, 1989, prevented the fulfillment of these plans.

We base these calculations on the assumption that the flow pattern under turbulent conditions consists of a turbulent core separated from the tube wall by a very thin laminar flow layer. We assume that the diffusion constant and viscosity within the turbulent core are uniform, and our essential task will be to calculate from experimental data:

(1) the core radius, r_t , as a fraction of the tube radius, r_0 :

$$r_t = \rho r_0 ; \rho < 1;$$

(2) the core viscosity, μ_t , as a function of the known laminar flow viscosity, μ_0 :

$$\mu_t = m\mu_0 ; m > 1;$$

(3) the core diffusivity, D_t , as a function of the known laminar flow diffusion constant, D_0 :

$$D_t = d D_0 ; d > 1.$$

Implied is also the postulate that ρ , m and d are essentially functions of the Reynolds number, Re ; fortuitously, the Reynolds number is an invariant within the tube as we pass from the high-pressure inlet side to the low-pressure outlet side.

We shall assume that the resistance to mass transfer in the fixed phase, the term,

$$\frac{k^3}{(1+k)^2}$$

in eqn. 22a in a previous paper¹⁴ is negligible, although it will be included in the mathematical derivations.

The pattern of the calculations will be to obtain three equations from which to calculate ρ , m and d under identical flow conditions (inclusion of the mass transfer term would require a fourth equation):

- (1) the flow resistance equation;
- (2) an equation connecting the observed HETP, h_0 , with the postulated ρ , m and d in the absence of retention ($k = 0$);
- (3) another equation connecting the observed HETP with ρ , m and d in the presence of some nominal retention, *e.g.*, $k = 1$.

The checks of the calculation should be:

- (1) under the same flow conditions predict and verify h for different retentions, k ;
- (2) under various flow conditions observe the variations of ρ , m and d as functions of Re .

The flow resistance equation

The average carrier gas velocity, in cm s^{-1} , in a tube of length L , in cm, for the case of laminar flow, is given by

$$u_0 = \frac{p_i^2 - p_o^2}{16p_o\mu L} \cdot r_0^2$$

where p_i and p_o are the inlet and outlet pressure and μ is the molecular dynamic viscosity, in poise ($\text{g cm}^{-1} \text{s}^{-1}$).

In the case of turbulent flow, designating $r_t = \rho r_0$, the radius of the turbulent core, the gas velocity in a point in the thin laminar flow region, at a distance r from the tube centre ($r > r_t$), will be given by

$$u = \frac{p_i^2 - p_o^2}{8p_o\mu L} (r_0^2 - r^2) \quad (\text{A1})$$

and the velocity within the turbulent core will be given by

$$u = \frac{p_i^2 - p_o^2}{8p_o L} \left(\frac{r_0^2 - r_t^2}{\mu} + \frac{r_t^2 - r^2}{\mu_t} \right) \quad (\text{A2})$$

The average velocity will be given by

$$u_0 = \frac{p_i^2 - p_o^2}{16p_o L r_0^2} \left(\frac{r_0^4 - r_t^4}{\mu} + \frac{r_t^4}{\mu_t} \right) \quad (\text{A3})$$

and the total flow will be given by

$$F_t = \pi \cdot \frac{p_i^2 - p_o^2}{16p_o L} \left(\frac{r_0^4 - r_t^4}{\mu} + \frac{r_t^4}{\mu_t} \right) \quad (\text{A3a})$$

$$= \pi \cdot \frac{(p_i^2 - p_o^2)r_0^4}{16p_o\mu L} \left[1 - \left(1 - \frac{1}{m} \right) \rho^4 \right] \quad (\text{A3b})$$

As velocities, flows and the HETP (h) can be fairly accurately determined, whereas, p_i , p_o and u cannot, the experimental procedure should consist in taking a tube of much greater length, sL , where $s \gg 1$, and, applying the same pressure differential across it, determine the velocity and flow, which are given by

$$u_L = \frac{(p_i^2 - p_o^2)r_0^2}{16p_o\mu s L} \quad (\text{A3c})$$

$$F_L = \pi \cdot \frac{(p_i^2 - p_o^2)r_0^4}{16p_o\mu s L} \quad (\text{A3d})$$

from which r_0 can be determined if required.

From eqns. A3a, b and d, we obtain

$$1 - \left(1 - \frac{1}{m}\right) \rho^4 = \frac{F_t}{sF_L} \quad (\text{A4})$$

F_t , F_L and s are determined by direct measurements and eqn. A4 is the first of the three equations needed.

The diffusion equations – laminar flow

These equations are tedious to manipulate, and the general attack used will be first illustrated for the case of laminar flow.

We consider a chromatographic tube of length L and radius r_0 with a retentive layer of thickness Δr , with a partition coefficient C and a diffusion constant D_L . The ratio of the total sample concentration to the concentration within the gas phase will be given by

$$\begin{aligned} \frac{r_0^2 + C[(r_0 + \Delta r)^2 - r_0^2]}{r_0^2} &= 1 + C \left[\left(1 + \frac{\Delta r}{r_0}\right)^2 - 1 \right] \\ &= 1 + k \end{aligned}$$

with

$$k = C \left[\left(1 + \frac{\Delta r}{r_0}\right)^2 - 1 \right]$$

or

$$\left(1 + \frac{\Delta r}{r_0}\right)^2 = 1 + \frac{k}{C} \quad (\text{A5})$$

The velocity at any point within the tube will be given by

$$u = 2u_0 \left(1 - \frac{r^2}{r_0^2}\right) \quad (\text{A6})$$

and the average sample velocity will be

$$\bar{u} = \frac{u_0}{1 + k} \quad (\text{A7})$$

We shall refer all calculations with respect to a system of coordinates moving with velocity \bar{u} in the direction of the current, and our approach, for both the laminar

and turbulent cases, will be to postulate a general sample concentration of the form

$$f = \frac{1}{\sqrt{t}} \exp \left[-\frac{[x - e(r)]^2}{4D't} \right] \quad (\text{A8})$$

and to apply to it the diffusion equation with the eventual aim of obtaining $e(r)$. This equation is usually given in the form

$$D\Delta^2 f = \frac{df}{dt} \quad (\text{A9})$$

which presupposes that D is a constant throughout. When D is not eqn. A9 should properly be written as

$$D\Delta^2 f + \text{grad } D \times \text{grad } f = df/dt \quad (\text{A9a})$$

but if D is constant within certain given zones, we may still use eqn. A9 within each zone, while introducing the boundary condition that at the interfaces of zones I and II, e.g., we should have

$$D \cdot \frac{df}{dS_I} = D_1 c \cdot \frac{df}{dS_{II}} \quad (\text{A9b})$$

where D and D_1 designate the respective diffusion constants of the two zones, S is some coordinate normal to the zones interface and c designates the ratio of concentrations which are in equilibrium across the interface.

The application of eqn. A9 to eqn. A8 yields one expression without $x - e(r)$ and one with it. The first is, after eliminating common coefficients,

$$D' = D \left[1 + \left(\frac{de}{dr} \right)^2 \right] \quad (\text{A10})$$

and the second is

$$D\Delta^2 e(r) = -(u - \bar{u}) \quad (\text{A11})$$

In the first expression, the dimensionless $(de/dr)^2$ represents a kind of entropy increase, and is therefore an extensive quantity which, with unity added, should be integrated throughout the tube cross-section and weighted everywhere by the appropriate diffusion times the partition coefficient when the latter differs from unity. The overall result, divided by the total effective tube cross-section, $r_0^2(1 + k)$ (π is omitted in practice), yields the desired value of D' when the flow has proceeded for some distance so that f has become substantially a Gaussian distribution for all r values.

The value of de/dr is obtained from the solutions of eqn. A11, which are

$$e(r) = -(1/D)\Delta^{-2}(u - u_0) \quad (\text{A12})$$

for the free-flowing zone, and

$$e(r) = (1/D_1)\Delta^{-2}\bar{u} \quad (\text{A12a})$$

for the fixed zone.

The values of de/dr obtained from this operation are, for the free-flowing inner part of the tube,

$$\frac{de}{dr} = -\frac{u_0}{2D} \left(\frac{1+2k}{1+k} \cdot r - \frac{r^3}{r_0^2} \right) \quad (\text{A13})$$

and for the fixed phase of thickness Δr ,

$$\frac{de}{dr} = \frac{u_0}{2(1+k)} \left[r - \frac{r_0^2(1+k/C)}{r} \right] \quad (\text{A13a})$$

It can be readily verified that these expressions satisfy eqns. A12 and A12a, respectively, in addition to the boundary condition of eqn. A9b, at the interface. Further, eqn. A13a satisfies the condition $de/dr = 0$ at the end of the fixed phase zone, where $r = r_0 + \Delta r$, which results from the proper choice of \bar{u} as given by eqn. A7.

Integration of $(de/dr)^2$ in the free-flowing zone yields a first contribution $\Delta D'_I$ to D' :

$$\Delta D'_I = \frac{1}{1+k} \left[D + \frac{u_0^2 r_0^2}{D} \cdot \frac{1+6k+11k^2}{48(1+k)^2} \right] \quad (\text{A14})$$

Integration and weighting of $(de/dr)^2$ in the stationary phase yields a second contribution, $\Delta D'_{II}$:

$$\Delta D'_{II} = \frac{C(u_0^2 r_0^2)}{2D_1(1+k)^3} \left[-\frac{k}{C} - \frac{3k^2}{4C^2} + \left(1 + 2 \cdot \frac{k}{C} + \frac{k^2}{C^2} \right) \frac{1}{2} \cdot \ln \left(1 + \frac{k}{C} \right) \right] \quad (\text{A14a})$$

When $k/C \ll 1$, $\ln(1 + k/C)$ can be replaced by the first three terms of its development and we obtain

$$\Delta D'_{II} = \frac{1}{1+k} \left[\frac{k^3}{12(1+k)^2} \cdot \frac{u_0^2 r_0^2}{C^2 D_1} \right] \quad (\text{A14b})$$

The parentheses in eqns. A14 and A14b correspond exactly to the parentheses on the left-hand side of eqn. 22a in a previous paper¹⁴, except for the limitation $k/C \ll 1$, which was not included at that time.

The diffusion equation —turbulent flow

For the discussion of this case we adopt again the flow distribution of eqn. A8 and set about determining $de(r)/dr$ for the three zones:

Zone I, the turbulent core, of radius $r_t = \rho r_0$, with viscosity $\mu_t = m\mu$ and diffusivity $D_t = dD$;

Zone II, the thin laminar layer next to the tube wall;

Zone III, the stationary phase, of thickness Δr , diffusivity D_1 , and with a concentration c times greater than in the free-flowing zones I and II.

The diffusion equations governing the concentration behaviour in these three zones can be solved as formerly and we obtain the following:

for Zone I, for $r < r_t$:

$$e = (1/D_t)\Delta^{-2} (u - \bar{u})$$

from which

$$\frac{de}{dr_1} = -\frac{p_i^2 - p_o^2}{32p_o D_t L r_0^2} \left[\frac{(1 + 2k)r_0^4 - 2(1 + k)r_0^2 r_t^2 + r_t^4}{(1 + k)\mu} \cdot r + \frac{2(1 + k)r_0^2 r_t^2 r - r_t^4 r - (1 + k)r_0^2 r^3}{(1 + k)\mu_t} \right] \tag{A15}$$

Observing the boundary condition:

$$\text{for } r = r_t, \quad D_t(de/dr_t) = D(de/dr_{II})$$

we find for Zone II, for $r_t < r < r_0$:

$$e = - (1/D)\Delta^{-2} (u - \bar{u})$$

from which

$$\frac{de}{dr_{II}} = -\frac{p_i^2 - p_o^2}{32p_o D L r_0^2} \left[\frac{(1 + 2k)r_0^4 + r_t^4}{(1 + k)\mu} \cdot r \cdot \frac{r_t^4}{(1 + k)\mu_t} \cdot r - \frac{r_0^2 r^3}{\mu} + \frac{r_0^2 r_t^4}{r} \left(-\frac{1}{\mu} + \frac{1}{\mu_t} \right) \right] \tag{A16}$$

And observing the boundary condition expressed by eqn. A9b, we find for the stationary zone:

$$r_0 < r < r_0 + r:$$

$$\frac{de}{dr_{III}} = \frac{p_i^2 - p_o^2}{32p_o D_1 L^2 r_0} \left[\frac{r_0^4 - r_t^4}{(1 + k)\mu} \cdot r + \frac{r_t^4}{(1 + k)\mu_t} \cdot r - \frac{(1 + k/C)r_0^6 - (1 + k/C)r_0^2 r_t^4}{(1 + k)\mu r} - \frac{1 + k/C}{\mu_t r} \right] \tag{A17}$$

As can be verified by inspection, the expressions given for de/dr in eqns. A15, A16 and A17 satisfy the three diffusion equations in their respective zones, plus the two boundary conditions at the I-II and II-III interfaces, plus the end condition:

$$\text{at } r = r_0 + \Delta r: \quad (de/dr_{\text{III}}) = 0$$

the latter being secured by our proper choice of \bar{u} .

When calculating the contributions of Zone I to D' , we first set $r = r_0 x$ and rewrite eqn. A15:

$$\frac{de}{dr} = -\frac{(p_i^2 - p_o^2)r_0^3}{32p_o r L d D} \left[\left(\frac{1 + 2k - 2(1+k)\rho^2 + \rho^4}{(1+k)} + \frac{2(1+k)\rho^2 - \rho^4}{(1+k)m} \right) x - \frac{x^3}{m} \right]$$

or, with eqn. A3c, and denoting by α_1 the coefficient of x within the brackets:

$$\alpha_1 = \frac{1 + 2k - 2(1+k)\rho^2 + \rho^4}{(1+k)} + \frac{2(1+k)\rho^2 - \rho^4}{(1+k)m}$$

$$\frac{de}{dr_1} = -\left(\frac{su_1 \cdot r_0}{2d \cdot D} \right) \left(\alpha_1 x - \frac{x^3}{m} \right) \quad (\text{A15a})$$

We calculate the contribution of Zone I to D' by applying

$$D' = D_i [1 + (de/dr)^2]$$

to eqn. A15a, to obtain

$$\begin{aligned} \Delta D'_I &= \frac{2}{r_1^2} \int_0^{r_1} dD \left[1 + \left(\frac{de}{dr} \right)_1^2 \right] r dr \\ &= \frac{2}{1+k} \cdot dD \left[\frac{\rho^2}{2} + \frac{s^2 u_1^2 r_0^2}{4d^2 D^2} \int_0^{\rho} \left(\alpha_1 x - \frac{x^3}{m} \right)^2 x dx \right] \\ &= \frac{2}{1+k} \left[dD \cdot \frac{\rho^2}{2} + \frac{s^2 u_1^2 r_0^2}{4dD} \left(\alpha_1^2 \frac{\rho^2}{4} - \frac{\alpha_1 \rho^6}{3m} + \frac{\rho^8}{8m^2} \right) \right] \end{aligned} \quad (\text{A18})$$

We now do likewise for Zone II and, setting again $r = r_0 x$, we rewrite eqn. A16:

$$\frac{de}{dr_{\text{II}}} = -\frac{(p_i^2 - p_o^2)r_0^3}{32p_o \mu L D} \left[\overbrace{\left(\frac{1 + 2k + \rho^4}{1+k} - \frac{\rho^4}{(1+k)m} \right)}^{\alpha_2} x - x^3 + \underbrace{\frac{\rho^4}{x} \left(-1 + \frac{1}{m} \right)}_{\beta_2} \right]$$

or, with eqn. A3c, and denoting by α_2 and β_2 the respective coefficients of x and $1/x$ within the brackets:

$$\frac{de}{dx_{II}} = -\frac{su_1r_0}{2D} [\alpha_2x - x^3 + \beta_2(1/x)] \tag{A16a}$$

We now calculate the contribution of Zone II to D' by applying eqn. A10 to eqn. A16a to obtain:

$$\begin{aligned} \Delta D'_{II} &= \frac{2}{r_1^2} \int_{r_1}^{r_0} D \left[1 + \left(\frac{de}{dr} \right)^2 \right] r dr = \frac{2}{1+k} \cdot D \left[\frac{1-\rho^2}{2} + \frac{s^2u_1^2r_0^2}{4D^2} \int_0^L \left(\alpha_2x - x^3 + \frac{\beta_2}{x} \right)^2 x dx \right] \\ &= \frac{2}{1+k} \left\{ D \cdot \frac{1-\rho^2}{2} + \frac{s^2u_1r_0^2}{4D} \left[\frac{\alpha_2^2(1-\rho^4)}{4} - \right. \right. \\ &\quad \left. \left. \frac{\alpha_2(1-\rho^6)}{3} + \alpha_2\beta_2(1-\rho^2) + \frac{1-\rho^8}{8} - \frac{\beta_2(1-\rho^4)}{2} + \beta_2^2 \ln(1/\rho) \right] \right\} \tag{A19} \end{aligned}$$

Theoretically we should determine the contribution of Zone III to D' , which will give us a term containing εD_1 in its denominator, but this would imply that this term is not negligible and constitutes a fourth parameter to be added to m , ρ and d , so that four equations would be required to determine all four parameters. This, however, implies the difficulty of using two columns in which the same sample has different k values but the same C^2D_1 term. At present it would appear more expeditious to make the measurements with columns having a negligible mass transfer term. Thus we would have only the difficulty of finding two columns which, for the same sample (to ensure that D_i for $k = 0$ is the same for both experiments) have appreciable k values but negligibly small terms containing $1/(C^2D_1)$. In conclusion, we form D' from the two contributions:

$$\Delta D'_I + \Delta D'_{II} = D' \tag{A20}$$

We measure D' experimentally and set the values found as equal to the quantities calculated from the known u_1 , r_0 and s and from the unknown m , ρ and d and, adding these two equations derived from the cases $k = 0$, for example, and $k = k$ (a known k) to the flow equation, determine the three unknown quantities just said.

SYMBOLS

- c Ratio of concentrations in two zones
- C Partition coefficient
- d Factor relating core diffusivity (D_i) to laminar flow diffusion constant (D_0) ($d > 1$)

D	Diffusion constant
D_L	Diffusion constant in the stationary phase
D_t	Core diffusivity
D_0	Laminar flow diffusion constant
f	Sample concentration function
F_t	Total flow
F_L	Flow through a tube
h	Height equivalent to a theoretical plate (HETP) in general
h_0	Observed HETP
k	Capacity factor (retention factor)
L	Tube length
m	Factor relating core viscosity (μ_t) to laminar flow viscosity (μ) ($m > 1$)
p_i	Inlet pressure
p_o	Outlet pressure
r	Distance from the tube centre ($r > r_t$)
r_0	Tube radius
r_t	Core radius
Δr	Thickness of retentive layer (liquid-phase film thickness)
Re	Reynolds number
s	Factor increasing tube length ($s \gg 1$)
S	A coordinate related to the interface of zones
t	Time
u	Carrier gas velocity
u_0	Average carrier gas velocity
\bar{u}	Average sample velocity
u_1	Velocity in a tube
α_1, α_2	Coefficients
β_2	Coefficient
ε	A factor
μ	Molecular dynamic viscosity
μ_t	Core viscosity
μ_0	Laminar flow viscosity
ρ	Factor relating core radius (r_t) to tube radius (r_0) ($\rho < 1$)

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