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UNSTEADY CONVECTIVE DIFFUSION IN CAPILLARY CHROMATOGRAPHY

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SUMMARY

An exact theory of unsteady convective diffusion in capillary chromatography is developed from first principles. Preliminary asymptotic results from the theory for large values of time provide rigorous justification for the Golay theory of capillary columns. The exchange coefficient, K_0, which arises from the analysis, is a new concept in capillary chromatography. K_0 represents the result of the interaction between the diffusion of solute to the wall and its removal by the retentive layer at the wall. The theory presented here allows one to predict concentration distributions directly from first principles but the results can also be used to calculate the moments of the solute distribution and other quantities of interest in chromatography.

INTRODUCTION

The idea of using very narrow columns for chromatographic analyses was first mentioned by Martin[1]. However, it was Golay[2] who announced the rather startling advantages offered by an open-tubular chromatographic column coated on the inside with a retentive layer. Kaiser[3], in his introduction, lists several advantages of this technique while Desty and co-workers[4-9] have demonstrated its usefulness and versatility in numerous areas of application. Some recent improvements and applications are contained in the works of Karoum and Sandler[10], Vestergaard and Jacobson[11], Mon[12], and Grob and Grob[13].

The distribution of solute in a capillary column is governed by the complex interactions between the mechanisms of axial convection, radial diffusion and exchange between the carrier fluid and the retentive layer. Theoretical analyses of solute behavior have been offered by Golay[2,14], Khan[15], and Giddings[16]. Golay adopted Taylor's[17] intuitive procedure in analyzing the dispersion of a pulse of solute in a coated capillary. The difference between Golay's and Taylor's works lies in the fact that Taylor's analysis applied to the case where there was no solute exchange between the flowing fluid and the capillary wall while Golay included this exchange, which is crucial to chromatographic separations. Khan[15] and Giddings[16] make Taylor-type

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assumptions in analyzing systems more general than the ones considered by Golay.

Aris[18] extended the method of moments he had presented in an earlier work[19] to analyze capillary chromatographic columns among other systems. He arrived at Golay's results in a more general form. Dayan and Levenspiel[20] analyzed the related problem of dispersion in pipes with adsorbing walls using Aris' method of moments.

Golay's[2,14] theoretical results on capillary columns enjoy widespread acceptance and usage in their design. However, his approach involves intuitive approximations similar to those made by Taylor[17]. Gill and Sankarasubramanian[21,22] showed that there is no need to make the approximations due to Taylor. They further showed that Taylor's[17] results are large-time asymptotes of a more general and exact theory of unsteady convective diffusion valid for all values of time which they developed from first principles. Sankarasubramanian and Gill[23] recently succeeded in extending this theory to interphase transfer problems. It is the purpose of this work to use their methodology in developing an exact theory of unsteady convective diffusion in capillary chromatographic systems valid, in principle, for all values of time and to show its relation to the asymptotic Golay theory.

We shall restrict ourselves to the problem of solute distribution in a coated capillary in which the coating is very thin and therefore offers negligible resistance to mass transfer so that instantaneous solute equilibrium may be assumed to exist between the retentive coating and the fluid adjacent to the wall. This is precisely the situation analyzed by Golay[2,14].

ANALYSIS

Consider the dispersion of solute initially distributed in a straight circular capillary of radius R. Let the fluid in the capillary be in fully developed time-dependent parallel laminar flow described by the axial velocity $u = u(t,r)$ where t is time and r is the radial coordinate. Let the partition ratio for the particular solute and retentive coating under consideration be specified by k. Assuming angular symmetry and ignoring free convection effects, the local concentration of solute C, which is a function of time t, axial coordinate x and radial coordinate r will satisfy the convective diffusion equation

$$\frac{\partial C}{\partial t} + u(t,r)\frac{\partial C}{\partial x} = D\left(\frac{1}{r}\frac{\partial}{\partial r} r \frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial x^2}\right) \tag{1}$$

along with the initial condition

$$C(0,x,r) = C_0\,\psi_1(x)\,Y_1(r) \tag{2a}$$

where C_0 is a reference concentration. This initial condition is quite general and can account for the pulse or slug input encountered in chromatographic separations. Furthermore, it also allows for possible transverse non-uniformities in the initial condition which arise, for instance, when one injects a sample directly into a carrier fluid using a syringe. Following Golay[14], we may write the boundary condition at the wall as

$$-D\frac{\partial C}{\partial r}(t,x,R) = \frac{kR}{2}\frac{\partial C}{\partial t}(t,x,R) \tag{2b}$$

Further, since the amount of solute in the system is finite

$$C(t,\infty,r) = \frac{\partial C}{\partial x}(t,\infty,r) = 0 \tag{2c}$$

and by symmetry

$$\frac{\partial C}{\partial r}(t,x,0) = 0 \tag{2d}$$

Defining the dimensionless quantities

$$\tau = \frac{Dt}{R^2},\ X = \frac{Dx}{R^2u_0},\ y = \frac{r}{R},\ U(\tau,y) = \frac{u(t,r)}{u_0},\ Pe = \frac{Ru_0}{D} \text{ and } \theta = \frac{C}{C_0},$$

eqns. 1 and 2 may be rewritten as

$$\frac{\partial\theta}{\partial\tau} + U(\tau,y)\frac{\partial\theta}{\partial X} = \frac{1}{y}\frac{\partial}{\partial y}y\frac{\partial\theta}{\partial y} + \frac{1}{Pe^2}\frac{\partial^2\theta}{\partial X^2} \tag{3}$$

$$\theta(0,X,y) = \psi(X)\,Y(y) \tag{4a}$$

$$\frac{\partial\theta}{\partial y}(\tau,X,1) = -\frac{k}{2}\frac{\partial\theta}{\partial\tau}(\tau,X,1) \tag{4b}$$

$$\theta(\tau,\infty,y) = \frac{\partial\theta}{\partial X}(\tau,\infty,y) = 0 \tag{4c}$$

$$\frac{\partial\theta}{\partial y}(\tau,X,0) = 0 \tag{4d}$$

where $\psi(X) \equiv \psi_1(x)$ and $Y(y) \equiv Y_1(r)$, u_0 is a reference velocity, and C_0 is a reference concentration. The solution of eqns. 3 and 4 is now formulated as

$$\theta = \sum_{j=0}^{\infty} f_j(\tau,y)\frac{\partial^j\theta_m}{\partial X^j} \tag{5}$$

where the dimensionless average concentration θ_m is defined as

$$\theta_m(\tau,X) = 2\int_0^1 y\theta\,\mathrm{d}y \tag{6}$$

Integration of eqn. 3 across the cross-section of the tube followed by the introduction of eqn. 5 results in the generalized dispersion equation

$$\frac{\partial \theta_m}{\partial \tau} = \sum_{i=0}^{\infty} K_i(\tau) \frac{\partial^i \theta_m}{\partial X^i} \tag{7}$$

where the coefficients K_i are defined by

$$K_i(\tau) = \frac{\delta_{i2}}{Pe^2} + 2 \frac{\partial f_i}{\partial y}(\tau,1) - 2 \int_0^1 f_{i-1}(\tau,y)\, U(\tau,y)\, y \,\mathrm{d}y \quad (i = 0, 1, 2, \ldots) \tag{8}$$

Here $f_{-1} \equiv 0$ and δ_{ij} is the Kronecker delta function defined by

$$\left.\begin{array}{l} \delta_{ij} = 1, \quad i = j \\ \delta_{ij} = 0, \quad i \neq j \end{array}\right\} \tag{9}$$

Eqn. 7 is the exact equation satisfied by the average concentration distribution in a capillary chromatographic system. It is derived from first principles and differs significantly from previous "models" for this quantity. Some of these differences are detailed below.

(1) Golay[14] derived a model for θ_m which involved a term $\partial^2 \theta_m / \partial \tau\, \partial X$ and did not contain the term $K_0 \theta_m$, which arises naturally out of this analysis. The term $K_0 \theta_m$ accounts for the diffusional transport of solute to the capillary wall and the exchange of solute with the wall.

(2) The coefficients in the dispersion equation, K_i, are time-dependent even if the velocity field is steady because of the time dependence of the functions f_j. It can be seen that all the functions f_j approach asymptotic steady-state representations for large τ when the velocity field U is steady. These will result in constant asymptotic values for the K_i. In contrast, earlier models contained only constant coefficients, which restricts their validity automatically to large values of τ and steady flow.

It was shown by Gill and Sankarasubramanian[21] that the infinite series in eqn. 7 can be truncated after the term involving K_2 without resulting in serious error. This was also verified by Sankarasubramanian and Gill[23] for situations involving interphase transport. The validity of the truncation for the present problem will be examined later in this work. After performing the truncation, the mean concentration, θ_m, satisfies

$$\frac{\partial \theta_m}{\partial \tau} = K_0(\tau)\, \theta_m + K_1(\tau) \frac{\partial \theta_m}{\partial X} + K_2(\tau) \frac{\partial^2 \theta_m}{\partial X^2} \tag{10}$$

The solution of eqn. 10 for θ_m requires a knowledge of the coefficients K_0, K_1 and K_2 in addition to initial and boundary conditions on θ_m. From eqn. 8 it may be seen that this requires a determination of f_0, f_1 and f_2. To achieve this, the solution, eqn. 5, is substituted in eqn. 3. Upon using eqn. 7 to evaluate $\partial^{j+1} \theta_m / \partial \tau\, \partial X^j$ in terms of $\partial^i \theta_m / \partial X^i$ and subsequently matching coefficients of $\partial^i \theta_m / \partial X^i$ $(i = 0, 1, 2, \ldots)$, we arrive at the following set of partial differential equations for f_j

$$\frac{\partial f_j}{\partial \tau} = \frac{1}{y} \frac{\partial}{\partial y} y \frac{\partial f_j}{\partial y} - U(\tau,y) f_{j-1} + \frac{1}{Pe^2} f_{j-2} - \sum_{i=0}^{j} K_i f_{j-i} \quad (j = 0,1,2,\ldots) \tag{11}$$

Here

$$f_{-1} = f_{-2} \equiv 0 \tag{12}$$

The initial and boundary conditions on $f_j(\tau,y)$ and $\theta_m(\tau,X)$ may be obtained from eqns. 4 and 5 as

$$\left.\begin{aligned}
&f_j(0,y) = \frac{Y(y)}{2\int_0^1 y\,Y(y)\,\mathrm{d}y}\,\delta_{j0} \\
&\frac{\partial f_j}{\partial y}(\tau,0) = 0 \\
&-\frac{2}{k}\frac{\partial f_j}{\partial y}(\tau,1) = \frac{\partial f_j}{\partial \tau}(\tau,1) + \sum_{l=0}^{j} K_l(\tau) f_{j-l}(\tau,1)
\end{aligned}\right\} \quad (j = 0, 1, 2, \ldots) \tag{13}$$

and

$$\left.\begin{aligned}
&\theta_m(0,X) = 2\psi(X) \int_0^1 y\,Y(y)\,\mathrm{d}y \\
&\theta_m(\tau,\infty) = \frac{\partial \theta_m}{\partial X}(\tau,\infty) = 0
\end{aligned}\right\} \tag{14}$$

Also, eqn. 6, when introduced into eqn. 5, requires that

$$\int_0^1 f_j y\,\mathrm{d}y = \frac{1}{2}\delta_{j0} \quad (j = 0, 1, 2, \ldots) \tag{15}$$

Coefficient K_0

The function f_0 and the coefficient K_0 are independent of the velocity field and can be solved for immediately. These two quantities are intimately coupled, as may be observed from their defining equations. Hence, they have to be solved for simultaneously. Following the procedure developed by Sankarasubramanian and Gill[23] for uncoupling f_0 and K_0 and using the methods of Lowan[24], for handling systems with non-orthogonal characteristic functions, the solution of eqns. 11, 13 and 15 for $j = 0$ may be written as

$$f_0(\tau,y) = \frac{A_0 + \sum_{1}^{\infty} A_n J_0(\alpha_n y) \exp(-\alpha_n^2 \tau)}{A_0 + 2\sum_{1}^{\infty} \frac{A_n}{\alpha_n} J_1(\alpha_n) \exp(-\alpha_n^2 \tau)} \tag{16}$$

where

$$A_n = \frac{\int_0^1 y\,Y(y)\,J_0(\alpha_n y)\,\mathrm{d}y}{J_0^2(\alpha_n)\left(1 + k + \frac{\alpha_n^2 k^2}{4}\right)\int_0^1 y\,Y(y)\,\mathrm{d}y} \quad (n = 0, 1, 2, \ldots) \tag{17}$$

and the characteristic values α_n are solutions of the transcendental equation

$$2J_1(\alpha) + k\alpha J_0(\alpha) = 0 \tag{18}$$

and hence are parametrically dependent on the partition ratio k. From eqn. 8 for $i = 0$, $K_0(\tau)$ then may be written as

$$K_0(\tau) = -\frac{2\sum\limits_1^\infty A_n\alpha_n J_1(\alpha_n)\exp\left(-\alpha_n^2\tau\right)}{A_0 + 2\sum\limits_1^\infty \frac{A_n}{\alpha_n} J_1(\alpha_n)\exp\left(-\alpha_n^2\tau\right)} \tag{19}$$

From eqn. 19 it is seen clearly that the new coefficient K_0, which we shall refer to as the "exchange coefficient", depends on the nature of the initial solute distribution $Y(y)$ through the coefficients A_n, which are defined by eqn. 17. As pointed out earlier, it is independent of the nature of the velocity distribution.

As $\tau \to \infty$, eqns. 16 and 19 give the following asymptotes

$$\lim_{\tau\to\infty} f_0(\tau,y) = f_0(\infty,y) = 1 \tag{20}$$

$$\lim_{\tau\to\infty} K_0(\tau) = K_0(\infty) = 0 \tag{21}$$

Steady flow — asymptotic K_i

While we were able to solve for the time-dependent coefficient $K_0(\tau)$ in its entirety with relative ease, such is not the case with the higher-order coefficients. The equations for f_j and K_j are coupled intimately and are quite complex so that the task of obtaining the complete time-dependent behavior of these quantities seems formidable. However, it is clear from the defining equations that $f_j(\tau,y)$ and $K_j(\tau)$ have non-trivial steady states for the case of steady flow. Since it is sufficient to obtain the asymptotic steady-state representations of the first few coefficients K_i for the case of steady flow in order to establish the relation of the present exact approach to Golay's work, we shall proceed to do so. When the flow is steady

$$u(t,r) = u(r) = u_0\left(1 - \frac{r^2}{R^2}\right) \tag{22a}$$

Here u_0 is the centerline velocity which is chosen as the reference velocity in defining non-dimensional quantities earlier. From eqn. 22a and the definition of U

$$U(y) = 1 - y^2 \tag{22b}$$

The equations for the steady-state coefficients K_j and the steady-state functions $f_j(y)$ can be obtained from eqns. 8 and 11–13 by simply dropping the time derivative. The resulting equations for f_j and K_j of the same order are still coupled. However, they can be uncoupled quite simply and the final solution for $f_j(y)$ may be written as

$$f_j(y) = B_j + \frac{K_j}{4}y^2 + \int_0^y \frac{1}{\xi}\int_0^\xi \eta\left[(1-\eta^2)f_{j-1}(\eta) - \frac{1}{Pe^2}f_{j-2}(\eta) + \sum_{i=1}^{j-1} K_i f_{j-i}(\eta)\right] \mathrm{d}\eta\,\mathrm{d}\xi \quad (j = 1, 2, 3, \ldots) \tag{23a}$$

where

$$B_j = f_j(0) = -\frac{K_j}{8} + 2\int_0^1 y \int_0^y \frac{1}{\xi}\int_0^\xi \eta\left[\frac{1}{Pe^2}f_{j-2}(\eta) - (1-\eta^2)f_{j-1}(\eta) - \sum_{i=1}^{j-1} K_i f_{j-i}(\eta)\right] \mathrm{d}\eta\,\mathrm{d}\xi\,\mathrm{d}y \quad (j = 1, 2, 3, \ldots) \tag{23b}$$

and the steady-state K_j are given in terms of the functions f_i ($i = 1, 2, \ldots, j-1$) by

$$K_j = \frac{1}{1+k}\left[\frac{\delta_{j2}}{Pe^2} - 2\int_0^1 f_{j-i}\, y(1-y^2)\,\mathrm{d}y - k\sum_{i=1}^{j-1} K_i f_{j-i}(1)\right] \quad (j = 1, 2, 3, \ldots) \tag{24}$$

Starting with $f_0 = 1$, K_1 may be calculated immediately from eqn. 24. This value of K_1 may then be used in eqns. 23 to obtain $f_1(y)$. This procedure may be repeated indefinitely to generate as many of the constants K_j as required. Here we shall content ourselves with calculating just the first three coefficients. These are given by

$$K_1 = -\frac{1}{2(1+k)} \tag{25a}$$

$$K_2 = \frac{1}{1+k}\,\frac{1}{Pe^2} + \frac{1 + 6k + 11k^2}{192(1+k)^3} \tag{25b}$$

$$K_3 = -\left[\frac{k(1+4k)}{24(1+k)^3}\,\frac{1}{Pe^2} + \frac{1 + 10k + 44k^2 + 122k^3 + 177k^4}{23040(1+k)^5}\right] \tag{25c}$$

The functions $f_1(y)$ and $f_2(y)$, which were obtained at intermediate stages in the above calculation, are tabulated in the appendix.

Relation to adsorption on the wall

The present method of approach applies equally well to situations where the solute is adsorbed on the wall instead of being removed by a retentive layer. For such cases, if $W(t,x)$ is defined as the surface concentration on the wall, the following condition describes the fact that the solute flux at the wall causes an accumulation in the adsorbed layer.

$$-D\frac{\partial C}{\partial r}(t,x,R) = \frac{\partial W}{\partial t} \tag{26}$$

Further, if a linear adsorption isotherm is assumed

$$W(t,x) = k'\,C(t,x,R) \tag{27}$$

where k' is the equilibrium constant for adsorption. Eliminating W from eqns. 26 and 27 we get

$$-D\frac{\partial C}{\partial r}(t,x,R) = k'\frac{\partial C}{\partial t}(t,x,R) \tag{28}$$

and comparison of eqns. 2b and 28 reveals that they will be identical if the partition ratio k is replaced by $2k'/R$. All the other equations will be the same and hence the present results also apply to the dispersion of an initial solute distribution in a tube with an adsorbing wall if k is replaced in terms of k' as indicated above.

Solution for θ_m

The final step is to solve for the average concentration distribution, $\theta_m(\tau,X)$. Eqns. 10 and 14 can be solved quite easily once the nature of the initial distribution is specified. Here we shall consider a very common case that arises in chromatography with direct injection. Solute of mass M is introduced instantaneously at the plane $x = 0$ at time zero uniformly across a circle of radius aR concentric with the tube axis. In this case, we may take

$$C_0 = \frac{M}{\pi R^3 Pe} \tag{29}$$

$$\psi(X) \equiv \psi_1(x) = \frac{R\delta(x)\,Pe}{a^2} = \frac{\delta(X)}{a^2} \tag{30a}$$

$$\left.\begin{array}{l} Y_1(r) = 1,\ 0 \leqslant r < aR \\ Y_1(r) = 0,\ aR \leqslant r \leqslant R \end{array}\right\} \tag{30b}$$

(In eqn. 30a, $\delta(x)$ and $\delta(X)$ are Dirac delta functions.) The solution of eqns. 10 and 14 then may be written as

$$\theta_m(\tau,X) = \frac{1}{2\sqrt{\pi\xi}}\exp\left(\zeta - \frac{X_1^2}{4\xi}\right) \tag{31}$$

where

$$\zeta(\tau) = \int_0^\tau K_0(\eta)\,d\eta \tag{32a}$$

$$X_1(\tau,X) = X + \int_0^\tau K_1(\eta)\,d\eta \tag{32b}$$

and

$$\xi(\tau) = \int_0^\tau K_2(\eta)\,d\eta \tag{32c}$$

The procedure used for obtaining eqn. 16 for $f_0(\tau,y)$ allows one to deduce the following result

$$\exp\,[\zeta(\tau)] = A_0 + 2\sum_{1}^{\infty} \frac{A_n}{\alpha_n} J_1(\alpha_n) \exp\,(-\alpha_n^2\tau) \tag{33}$$

For large τ, the coefficient K_0 approaches zero and this explains why this term was never present in previous dispersion model descriptions of the average concentration. However, it can be clearly seen from the present exact approach that the entire time history of $K_0(\tau)$ is important. Eqn. 33 may be approximated for large τ by

$$\exp\,[\zeta(\tau)] \sim A_0 = \frac{1}{1+k} \tag{34}$$

Since the coefficients $K_1(\tau)$ and $K_2(\tau)$ approach non-zero steady-state values K_1 and K_2 given by eqns. 25a and 25b, the solution for θ_m for large τ may be approximated by

$$\theta_m(\tau,X) = \frac{1}{2\,(1+k)\sqrt{(\pi K_2\tau)}} \exp\left(-\frac{(X+K_1\tau)^2}{4K_2\tau}\right) \tag{35}$$

It should be clear, of course, that while the coefficients K_l have non-trivial steady-state values, the concentration distribution itself is inherently unsteady and that the steady-state concentration distribution is the trivial solution $\theta_m \equiv 0$. Eqn. 35 is an asymptotic result valid for large τ and does not represent a steady-state solution. It should be noted that this asymptotic solution is independent of non-uniformities in the initial distribution which have been attenuated by the process of convective diffusion.

For completeness, the formal solution of the generalized dispersion eqn. 7 along with eqns. 14 for the present system is reported here.

$$\theta_m(\tau,X) = \frac{\exp\,[\zeta(\tau)]}{2\pi} \int_{-\infty}^{\infty} \exp\,[-i\beta X_1 + \sum_{l=2}^{\infty} (-i\beta)^l \int_0^{\tau} K_l(\eta)\,\mathrm{d}\eta]\,\mathrm{d}\beta \tag{36}$$

In eqn. 36, $i = \sqrt{-1}$ and $\zeta(\tau)$ and $X_1(\tau,X)$ are defined by eqns. 32a and 32b.

Spatial moments

Golay's[14] results were presented in terms of spatial moments of the distribution. For comparison, the dimensionless spatial moments of the solute distribution in this work may be defined as follows.

$$\mu^{(0)} = \int_{-\infty}^{\infty} \theta_m(\tau,X)\,\mathrm{d}X \tag{37a}$$

$$\mu^{(1)} = \int_{-\infty}^{\infty} \theta_m X\,\mathrm{d}X \tag{37b}$$

$$\mu^{(j)} = \int_{-\infty}^{\infty} \theta_m\, X_1^{\,j}\,\mathrm{d}X_1 \quad (j = 2, 3, 4, \ldots) \tag{37c}$$

It may be noted that the second and higher-order moments are defined on the basis of the dimensionless moving coordinate system, X_1, defined in eqn. 32b, and hence are "central moments" of the distribution. Exact expressions for the moments may be obtained from the generalized dispersion eqn. 7 by multiplication of both sides by X^j or X_1^j as required and subsequent integration. Use of the initial condition, and the condition that the solute always is distributed in a finite region, leads to the following results for the first few moments.

$$\mu^{(0)} = \exp[\zeta(\tau)] \tag{38a}$$

$$\mu^{(1)} = -\mu^{(0)} \int_0^\tau K_1(\eta)\,\mathrm{d}\eta \tag{38b}$$

$$\mu^{(2)} = 2\mu^{(0)} \int_0^\tau K_2(\eta)\,\mathrm{d}\eta \tag{38c}$$

For large τ, eqns. 38 may be approximated by

$$\mu^{(0)} \approx \frac{1}{1+k} \tag{39a}$$

$$\mu^{(1)} \approx \frac{\tau}{2(1+k)^2} \tag{39b}$$

$$\mu^{(2)} \approx \frac{2\tau}{(1+k)^2}\left[\frac{1}{Pe^2} + \frac{1+6k+11k^2}{192(1+k)^2}\right] \tag{39c}$$

It may be observed that the dimensionless zeroth moment of the solute distribution, which is a measure of the total amount of solute in the fluid, starts out at unity and decays monotonically to the asymptotic value given in eqn. 39a. Golay[14], in his model, chose to normalize his distribution about the asymptotic zeroth moment. Hence, he obtained expressions for the higher moments in his work which, when expressed in dimensionless form, differ from eqn. 39 by a factor of $(1 + k)$. Otherwise, the large-time asymptotes of the present exact theory are identical to Golay's results thereby establishing the asymptotic nature of the Golay theory. The present results also differ from Aris's by a factor of $(1 + k)$ due to an entirely different reason. Aris included the solute in the retentive layer in his definition of the spatial moments and hence obtained a zeroth moment, which, initially normalized, never changed with time. It must be noted clearly that the moments reported in eqn. 39 correspond to the solute distribution in the flowing fluid.

DISCUSSION

In contrast to previous analyses of capillary chromatographic systems which employed intuitive approximations, the present procedure allows one to write exact solutions of the equation of convective diffusion. While this work is limited by the complexity of the system which has made it possible only to obtain asymptotic representations of the higher order f_j and K_j, this is not a restriction on the method itself. The theory is capable of predicting system behavior for all values of time right from zero without recourse to arbitrary approximations.

The exchange coefficient K_0 arises naturally out of the analysis in describing average concentration distributions in interphase transport problems (Sankarasubramanian and Gill[23]), and, to this author's knowledge, is new in capillary chromatography. One may note that K_0 approaches the value zero asymptotically for large time for all values of the partition ratio k. Further, this asymptote is independent of the initial solute distribution. However, the short-lived K_0 leaves a permanent effect on the solution in the form of the term $1/(1 + k)$ in the asymptotic solution, eqn. 35.

It is interesting to observe the behavior of the new coefficient K_0 as a function of τ and Figs. 1–3 depict this for different values of the partition ratio k and the dimensionless pulse radius, "a". These data are calculated from eqn. 19. For the initial distribution given by eqn. 30b, the coefficients A_n are obtained from eqn. 17 as

$$A_n = \frac{8J_1(\alpha_n a)}{a\alpha_n J_0^2(\alpha_n)\,(4 + 4k + \alpha_n^2 k^2)} \quad (n = 1, 2, 3, \ldots) \tag{40a}$$

For large values of k, the following alternate expression is more useful:

$$A_n = \frac{2\alpha_n J_1(\alpha_n a)}{aJ_1^2(\alpha_n)\left(\frac{4}{k^2} + \frac{4}{k} + \alpha_n^2\right)} \quad (n = 1, 2, 3, \ldots) \tag{40b}$$

K_0 represents the combined effect of diffusion of solute to the wall and the exchange of solute between the stationary and mobile phases at the wall. When a balance is achieved between the two as τ becomes large, K_0 approaches the value zero. K_0 is mostly negative, because, during the period of its existence, solute is being removed from the system by the retentive layer at the wall and hence the term $K_0\,\theta_m$ in eqn. 7 should be a sink term. Since K_0 does not depend on the velocity field for its existence, the simplest way to visualize it is to imagine a stationary system with an initial distribution similar to the one in the present problem but uniform axially. Such a system is defined in mathematical terms by the equations for f_0. K_0 is a linear multiple of the concentration gradient existing at the wall in that system.

In Fig. 1, K_0 is plotted as a function of τ for $k = 0.5$. $a = 1$ corresponds to a pulse initially uniform across the entire cross-section. The essentially infinite concentration gradient which initially exists at the tube wall is the cause of the large absolute values of K_0 for small τ in this case. Continuous removal of solute by the retentive layer at the wall and resupply by diffusion result in the observed monotonic behavior of K_0 for $a = 1$. When the initial pulse occupies the region $r = 0 - 0.95R$ uniformly, the initial solute gradient at the wall is zero and K_0 starts at an initial value of zero. The figure shows its behavior from $\tau = 10^{-4}$ from which it can be inferred that, initially, relatively large amounts of solute are transferred to the wall region and to the retentive layer. This causes the retentive layer to transfer some solute back to the fluid which causes the positive values of K_0 in the region $10^{-4} \leqslant \tau \leqslant 1.4 \times 10^{-4}$. Resupply of solute by diffusion makes K_0 reach negative values again until, finally, the balance is found and $K_0 \rightarrow 0$.

For smaller values of "a", Fig. 2 shows the behavior of K_0 as a function of τ. The plots have been made on an expanded scale and the cases $a = 0.95$ and 1 are also included for comparison. It is evident from the figures that K_0 undergoes adjustment as the balance between the bulk fluid diffusion and the wall processes is being achieved.

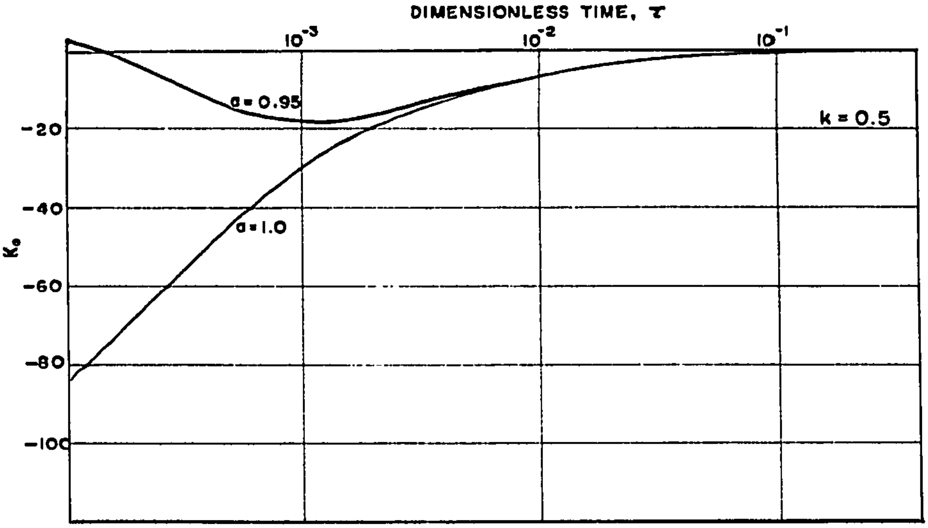

Fig. 1. Plots of the dimensionless exchange coefficient, K_0, against dimensionless time, τ, from eqn. 19 for $a = 1.0$ and 0.95; $k = 0.5$.

One may note that for similar values of "a", the solute undergoes dilution by the time it reaches the wall and hence wall concentrations and concentration gradients are smaller, resulting in smaller values of K_0.

In all the above cases, it may be observed that $K_0 \rightarrow 0$ for $\tau \sim 0.4$ to 0.6. The smaller the value of "a", the larger is the time taken for the asymptote to be reached.

Fig. 3 shows the behavior of $K_0(\tau)$ for larger values of k, *viz.*, $k = 50$ and 500. It is seen from the figure that for up to $\tau = 0.1$, the behavior of K_0 changes very little,

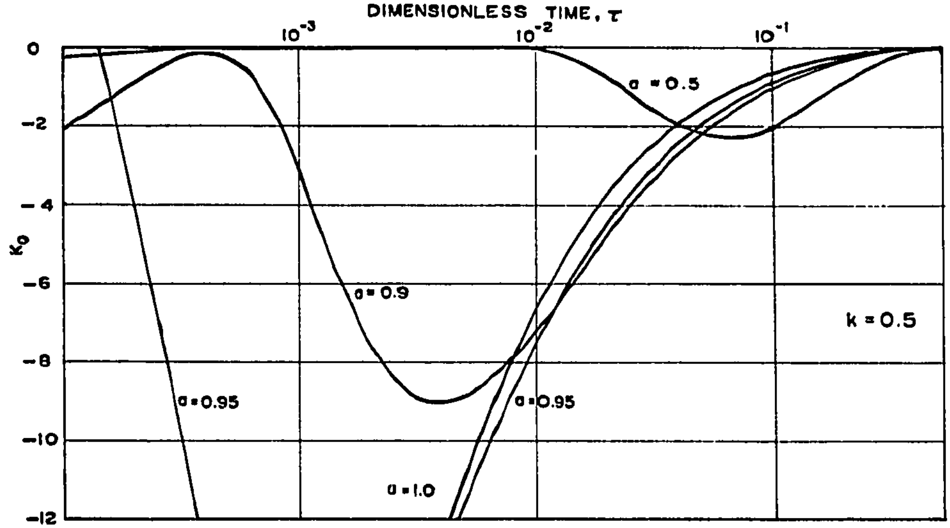

Fig. 2. Plots of the dimensionless exchange coefficient, K_0, against dimensionless time, τ, from eqn. 19 for $a = 1.0$, 0.95, 0.9 and 0.5; $k = 0.5$.

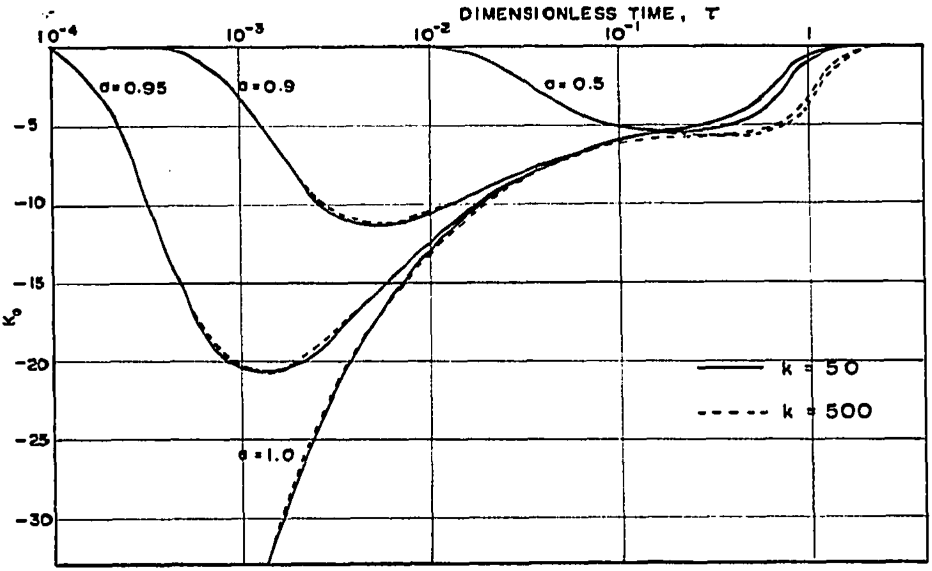

Fig. 3. Plots of the dimensionless exchange coefficient, K_0, against dimensionless time, τ, from eqn. 19 for $a = 1.0$, 0.95, 0.9 and 0.5; $k = 50$ and 500.

indicating that its dependence on τ has reached an asymptotic form for large k. However, there is a significant difference between the two sets of results in the region $\tau = 0.1$–2. It may be observed from the figure that there is a region of τ here over which K_0 is substantially constant after which it decays to zero. This curious phenomenon may be explained from an examination of eqn. 19, which reveals that, normally for sufficiently large τ, K_0 may be written approximately as

$$K_0(\tau) \approx -\frac{A_1 \alpha_1 J_1(\alpha_1)\, \mathrm{e}^{-\alpha_1^2 \tau}}{\frac{A_0}{2} + \frac{A_1}{\alpha_1} J_1(\alpha_1)\, \mathrm{e}^{-\alpha_1^2 \tau}} \tag{41}$$

However, for large k, A_0 can be very small so that there is a region of τ over which the first term in the denominator of eqn. 41 is negligible compared to the second and

$$K_0(\tau) \sim -\alpha_1^2 \tag{42}$$

of course, as τ becomes larger, the term involving A_0 becomes quite important and $K_0(\tau)$ ultimately decays to zero. From eqn. 34 for A_0, it is also clear that as k increases, this region over which K_0 is constant extends for larger values of τ and K_0 decays to zero much later as is verified by Fig. 3.

It should be pointed out at this stage that for typical gas-phase chromatographic systems, the real time taken for K_0 to approach zero would be in the order of a few seconds at the most because of the relatively large values of gas-phase diffusivities. However, in a liquid-phase separation, this time can be as high as half an hour since the diffusivities are smaller by three orders of magnitude.

The dimensionless zeroth-order moment of the solute distribution, $\mu^{(0)}$, is the ratio of the total amount of solute present in the flowing fluid at any time to the total amount of solute originally introduced into the system. Initially, $\mu^{(0)}$ is equal to unity. As solute is transferred into the retentive layer at the wall, $\mu^{(0)}$ decreases and ultimately approaches a steady asymptotic value of $1/(1+k)$ for large τ as $K_0 \to 0$. This signifies the attainment of overall equilibrium between the solute present in the flow and that in the retentive layer. Figs. 1–3 show that the time required for this asymptote to be reached for practical purposes increases for increasing k. Of course, even though overall equilibrium has been achieved, locally, near the tail end of the distribution, solute will be continually transferred from the retentive layer to the bulk fluid because of relatively lower solute concentrations in the flow. Near the front, the opposite will be true.

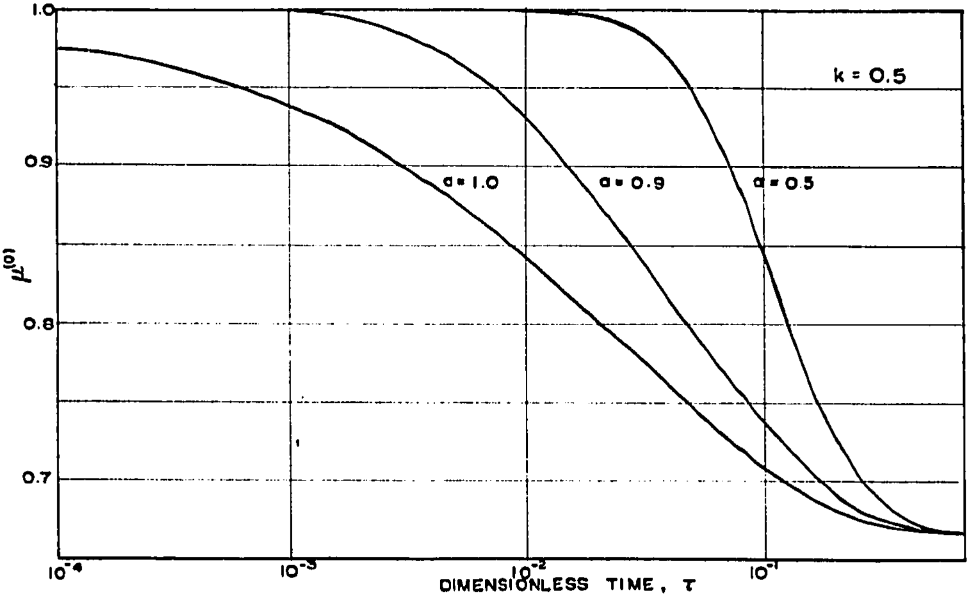

Fig. 4. Plots of the dimensionless zeroth moment, $\mu^{(0)}$, against dimensionless time, τ, for $a = 1.0$, 0.9 and 0.5; $k = 0.5$.

$\mu^{(0)}$, which is defined by eqns. 38a and 37a, may be calculated from eqn. 33. This expression may be recognized as the denominator in eqn. 19 for K_0 and hence is obtained during the process of computing K_0. Figs. 4 and 5 are plots of $\mu^{(0)}$ against dimensionless time, τ. In Fig. 4, $\mu^{(0)}$ is plotted for $k = 0.5$ over a range of values of the dimensionless pulse radius, "a". It is seen that for smaller values of "a", the solute takes time to diffuse to the wall and get transferred to the retentive layer. Hence $\mu^{(0)}$ remains close to unity for longer periods of time since the start of the process for smaller values of "a". Ultimately, independent of the nature of the initial distribution, overall equilibrium is reached by $\tau \approx 0.6$. Fig. 5 shows the behavior of $\mu^{(0)}$ for larger values of k and it may be observed that up to $\tau \approx 0.1$, $\mu^{(0)}$ shows no change with increasing k indicating that $k = 50$ is large enough for $\mu^{(0)}$ to exhibit asymptotic behavior for large k. For $\tau > 0.1$, different k values result in differences in the plots due to the differences in the lengths of the constant K_0 regions discussed earlier. Also, the

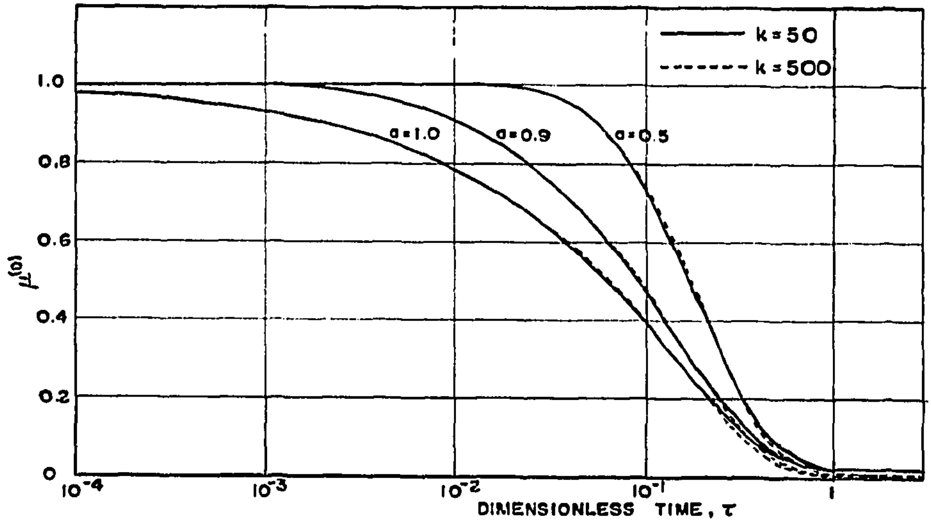

Fig. 5. Plots of the dimensionless zeroth moment, $\mu^{(0)}$, against dimensionless time, τ, for $a = 1.0$, 0.9 and 0.5; $k = 50$ and 500.

figures show that the large-time asymptotes are reached for larger values of τ as k increases and that the asymptotic values themselves are smaller for larger k.

Table I shows values of K_1, K_2 and K_3 calculated using eqns. 25 for various values of the partition ratio, k. The Peclet number is left in as a parameter. It may be observed from the equations that as $k \to 0$, K_1, K_2 and K_3 approach the following limiting values in agreement with the results of Gill and Sankarasubramanian[22] for the case of no interphase transport.

$$K_1 \to -\frac{1}{2} \tag{43a}$$

$$K_2 \to \frac{1}{Pe^2} + \frac{1}{192} \tag{43b}$$

$$K_3 \to -\frac{1}{23040} \tag{43c}$$

TABLE I

ASYMPTOTIC COEFFICIENTS K_1, K_2 AND K_3 FOR VARIOUS VALUES OF k

k	K_1	K_2	K_3
0	-0.5	$\frac{1}{Pe^2} + (5.208 \times 10^{-3})$	$-\ 4.340 \times 10^{-5}$
0.5	-3.333×10^{-1}	$\frac{6.667 \times 10^{-1}}{Pe^2} + (1.042 \times 10^{-2})$	$-\ \frac{1.852 \times 10^{-2}}{Pe^2} - (2.476 \times 10^{-4})$
5	-8.333×10^{-2}	$\frac{1.667 \times 10^{-1}}{Pe^2} + (7.378 \times 10^{-3})$	$-\ \frac{2.025 \times 10^{-2}}{Pe^2} - (7.090 \times 10^{-4})$
50	-9.804×10^{-3}	$\frac{1.961 \times 10^{-2}}{Pe^2} + (1.092 \times 10^{-3})$	$-\ \frac{3.157 \times 10^{-3}}{Pe^2} - (1.411 \times 10^{-4})$
500	-9.980×10^{-4}	$\frac{1.996 \times 10^{-3}}{Pe^2} + (1.140 \times 10^{-4})$	$-\ \frac{3.315 \times 10^{-4}}{Pe^2} - (1.523 \times 10^{-5})$

In the limit as $k \to \infty$, it can be shown that all the coefficients K_i ($i = 0, 1, 2, \ldots$) and the functions $f_j(y)$ ($j = 1, 2, 3, \ldots$) approach zero.

Examination of Table I reveals that for large values of time, the truncation of the dispersion equation at the term involving K_2 is quite justified for small values of the partition ratio, k. For large k, such truncation may not be very safe and the actual importance of including the term involving K_3 can only be assessed by comparing exact solutions of the dispersion equation with and without the additional term.

The height equivalent to a theoretical plate (HETP)

The HETP is a widely used quantity in chromatography. This is related to the asymptotic coefficients K_1 and K_2 as follows.

$$H = \frac{2\,Pe\,K_2\,R}{(-K_1)} \tag{44}$$

CONCLUSIONS

An exact procedure, valid for all values of time, is formulated for analyzing convective diffusion in capillary chromatographic systems. Preliminary asymptotic results derived from the theory for large values of time provide rigorous justification for the classical results due to Golay[14].

The exchange coefficient, K_0, is a new quantity in the dispersion equation for a capillary chromatographic column. The behavior of this coefficient is examined in detail. It is also shown in this work that the higher-order terms in the dispersion equation may become important for large values of the partition ratio, k.

The methods developed here can be used to calculate quantities of interest in chromatography such as the height of a theoretical plate and the moments of the solute distribution.

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NOMENCLATURE

A_n = Expansion coefficients defined by eqn. 17
a = Dimensionless radius of the pulse, $0 \leqslant a \leqslant 1$
B_j = Coefficients defined in eqn. 23b
C = Concentration of solute, g/cm^3
C_m = Area-average concentration, g/cm^3; $C_m = {}_0\int^R Cr\mathrm{d}r / {}_0\int^R \mathrm{d}r$
C_0 = Reference concentration, g/cm^3
D = Molecular diffusivity, cm^2/sec
f_j = Dimensionless functions defined by eqns. 11–13 and 15
H = Height equivalent to a theoretical plate, cm
J_0 = Bessel function of the first kind of order 0
J_1 = Bessel function of the first kind of order 1
K_i = Dimensionless coefficients in the generalized dispersion equation defined in eqn. 8

k = Partition ratio (dimensionless)
k' = Equilibrium constant for adsorption, cm
M = Total amount of solute in the initial distribution, g
Pe = Peclet number, Ru_0/D
R = Tube radius, cm
r = Radial coordinate, cm
t = Time, sec
U = Dimensionless axial velocity, u/u_0
u = Axial velocity, cm/sec
u_0 = Reference velocity, cm/sec
W = Concentration in the adsorbed layer on the inner surface of the conduit, g/cm^2
X = Dimensionless axial coordinate, Dx/R^2u_0
X_1 = Dimensionless translating axial coordinate defined in eqn. 32b
x = Axial coordinate, cm
$Y(y)$ = Radial dependent part of the initial distribution
$Y_1(r) \equiv Y(y)$
y = Dimensionless radial coordinate, r/R
α_n = Eigenvalues defined by eqn. 18
β = Fourier variable
ζ = Dimensionless function defined by eqn. 32a
η = Dummy variable of integration
θ = Dimensionless concentration, C/C_0
θ_m = Dimensionless average concentration, C_m/C_0
$\mu^{(j)}$ = Dimensionless moments of the solute distribution defined in eqns. 37
ξ = Dimensionless function defined by eqn. 32c
τ = Dimensionless time, Dt/R^2
$\psi(X)$ = Axial dependent part of the initial distribution
$\psi_1(x) \equiv \psi(X)$

APPENDIX

The steady-state functions $f_1(y)$ and $f_2(y)$ are given below.

$$f_1(y) = -\frac{2+5k}{48(1+k)} + \frac{1+2k}{8(1+k)}y^2 - \frac{1}{16}y^4 \tag{A.1}$$

$$\begin{aligned} f_2(y) = {} & \frac{k}{4(1+k)Pe^2}\left(\frac{1}{2} - y^2\right) + \frac{31+173k+313k^2+351k^3}{46080(1+k)^3} - \\ & - \frac{3+16k+27k^2+20k^3}{768(1+k)^3}y^2 + \frac{5+19k+17k^2}{768(1+k)^2}y^4 - \\ & - \frac{5(1+2k)}{1152(1+k)}y^6 + \frac{1}{1024}y^8 \end{aligned} \tag{A.2}$$

REFERENCES

1 A. J. P. Martin, in D. H. Desty (Editor), *Vapor Phase Chromatography*, Butterworths, London, 1957, p. 2.

2 M. J. E. Golay, in V. J. Coates, H. J. Noebels and I. S. Fagerson (Editors), *Gas Chromatography*, Academic Press, New York, 1958, p. 1.
3 R. Kaiser, *Gas Phase Chromatography, Vol. II, Capillary Chromatography* (translated by P. H. Scott), Butterworths, London, 1963.
4 D. H. Desty, A. Goldup and B. H. F. Wyman, *J. Inst. Petrol.*, 45 (1969) 287.
5 D. H. Desty and A. Goldup, in R. P. W. Scott (Editor), *Gas Chromatography 1960*, Butterworths, Washington, 1960, p. 162.
6 D. H. Desty and W. T. Swanton, *J. Phys. Chem.*, 65 (1961) 766.
7 D. H. Desty, A. Goldup, G. R. Lockhurst and W. T. Swanton, in M. Van Swaay (Editor), *Gas Chromatography 1962*, Butterworths, Washington, 1962, p. 67.
8 D. H. Desty, *Advan. Chromatogr.*, 1 (1965) 199.
9 D. H. Desty, *Mem. Soc. Endocrinol.*, 16 (1967) 7.
10 F. Karoum and M. Sandler, *Clin. Chim. Acta*, 32 (1971) 391.
11 P. Vestergaard and E. Jacobson, *J. Chromatogr.*, 50 (1970) 239.
12 T. R. Mon, *Res. Develop.*, 22, No. 12 (1971) 14.
13 K. Grob and A. Grob, *Chromatographia*, 5, No. 1 (1972) 3.
14 M. J. E. Golay, in D. H. Desty (Editor), *Gas Chromatography*, Butterworths, London, 1958, p. 36.
15 M. A. Khan, in M. Van Swaay (Editor), *Gas Chromatography 1962*, Butterworths, Washington, 1962, p. 3.
16 J. C. Giddings, *Dynamics of Chromatography, Part I, Principles and Theory*, Marcel Dekker, New York, 1965, p. 153.
17 G. I. Taylor, *Proc. R. Soc. London*, A219 (1953) 186.
18 R. Aris, *Proc. R. Soc. London*, A252 (1959) 538.
19 R. Aris, *Proc. R. Soc. London*, A235 (1956) 67.
20 J. Dayan and O. Levenspiel, *Ind. Eng. Chem. Fund.*, 8 (1969) 840.
21 W. N. Gill and R. Sankarasubramanian, *Proc. R. Soc. London*, A316 (1970) 341.
22 W. N. Gill and R. Sankarasubramanian, *Proc. R. Soc. London*, A322 (1971) 101.
23 R. Sankarasubramanian and W. N. Gill, *Proc. R. Soc. London*, A333 (1973) 115.
24 A. N. Lowan, *Phil. Mag., Ser. 7*, 17, No. 114 (1934) 849.